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Guideline for Using the Carbon-Bond Mechanism in City-Specific EKMA (Empirical Kinetics Modeling Approach)

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The document describes how to use the Carbon Bond 3 (CB-3) chemical mechanism in the city-specific EKMA model as a means for estimating emission control requirements needed to demonstrate attainment of the ozone NAAQS. Topics addressed include (a) an overview of the CB-3 mechanism, (b) procedures for applying the CB-3/EKMA model, and (c) special computer considerations to be taken into account when using CB-3 with city-specific EKMA.

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Office Of Air Quality Planning And Standards
Office Of Air And Radiation
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Research Triangle Park, North Carolina 27711

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1.0 INTRODUCTION

In March of 1981, the U.S. Environmental Protection Agency (EPA) issued guidelines for applying the city specific Empirical Kinetics Modeling Approach (EKMA).[1] EKMA is a procedure that can be used to estimate reductions in emissions of Volatile Organic Compounds (VOCs) that are needed to achieve the National Ambient Air Quality Standard (NAAQS) for ozone. Application of city-specific EKMA according to the March 1981 guidelines entails using the Ozone Isopleth Plotting Package (OZIPP) to relate peak ozone concentrations to its precursors - Nonmethane Organic Compounds (NMOC) and Oxides of Nitrogen (NO_x).[2,3] OZIPP is a computer program that incorporates a simplified trajectory model and a chemical kinetics mechanism (known as the DODGE mechanism) that mathematically simulate ozone formation. Since the issuance of the March 1981 guidelines, the use of other chemical mechanisms with EKMA has been suggested.[4,5] In response, supplemental guidance on using other mechanisms was circulated to EPA Regional Offices in December of 1981.[6] The supplemental guidance contained generalized recommendations regarding the application of other mechanisms, but did not provide specific details on how any one particular mechanism might be incorporated in an EKMA modeling analysis. The purpose of this document is to provide more specific information regarding the use of one alternative mechanism - the Carbon-Bond III mechanism (CB-3) developed by Systems Applications, Incorporated.[7]

The March 1981 guidelines dealt exclusively with using the DODGE chemical mechanism and the EKMA technique. Those guidelines contained recommended approaches for formulating OZIPP input variables and applying EKMA to estimate the VOC emission reduction needed to achieve the ozone NAAQS. Many of these recommendations are appropriate for the CB-3 mechanism as well. In a few instances, however, the recommendations were based on the results of sensitivity tests conducted with the DODGE mechanism. Because the CB-3 and DODGE mechanisms do not always exhibit the same sensitivity to a particular model input variable, some of the March 1981 recommendations need to be modified when CB-3 is used with EKMA. This document focuses primarily on those modifications that are needed to use the CB-3 mechanism with EKMA in an appropriate manner, but also summarizes the recommendations that remain unchanged.

The recommended approach for applying EKMA with the CB-3 mechanism (hereafter referred to as EKMA/CB-3) parallels the one outlined in the March 1981 guidelines for using EKMA/DODGE. As a consequence, the format of this document is similar to that of the 1981 guidelines. Procedures are recommended for transforming available emissions and aerometric data into model input values. Alternative procedures are suggested for those cases in which sufficient information is available to warrant their use. Also, every effort has been made to provide so called "default" values that can be used in the event of missing data. Because of the similarities between an EKMA/CB-3 and EKMA/DODGE analysis, this document is intended to serve as a companion to the March 1981 guidelines. The reader will more than likely find it useful to refer to the 1981 guidelines for discussions on the concepts underlying the modeling analysis or for details on any particular portion of the modeling approach.

As discussed in the March 1981 guidelines, the EKMA technique is applied by using the OZIPP computer program that internally incorporates the DODGE mechanism. While OZIPP could be modified to replace the DODGE mechanism with CB-3, extensive revisions to the computer code would be required. However, an alternative program that accepts as input any chemical mechanism is available. This program, Ozone Isopleth Plotting With Optional Mechanisms (OZIPM) is very similar in structure to OZIPP, but provides the flexibility needed for dealing with optional mechanisms.[8] Since it is considerably easier to deal with OZIPM rather than modify OZIPP, the discussions that follow will focus exclusively on using the CB-3 mechanism with the OZIPM program.

The remainder of this document is divided into three chapters. Chapter 2.0 contains a discussion of the CB-3 mechanism and its relationship to the OZIPM program. Chapter 3.0 describes the modifications to the March 1981 guidelines that are needed for an EKMA/CB-3 application. Finally, Chapter 4.0 illustrates how the model inputs described in Chapters 2 and 3 are actually used with OZIPM in order to apply the EKMA technique.

One final point should be made concerning the evolution of the recommendations contained herein. As noted previously, the CB-3 mechanism was developed by SAI. Because of their unique expertise with CB-3 and their familiarity with EKMA, EPA contracted with SAI to develop a methodology for using CB-3 within the city-specific EKMA framework.[9] The recommended methodology was used by the EPA to formulate an initial set of guidelines which were discussed with representatives of EPA, SAI and the University of North Carolina (UNC). Subsequent to these discussions, the guidelines were revised, and then circulated to the same representatives, and to other interested parties for further comments. The final guidelines thus represent a synthesis of ideas expressed by a number of interested groups.

2.0 THE CB-3 MECHANISM

As the name implies, CB-3 is the third in a series of evolving chemical kinetics mechanisms. Each of the successive carbon bond mechanisms contains revisions that reflect increased knowledge of the photochemistry leading to ozone formation. The CB-3 mechanism is currently the most recent version of that generic series. It has been designed to simulate laboratory smog chamber experiments using detailed data bases, as well as atmospheric situations in which much less information is typically available. While a comprehensive discussion on the scientific basis of the CB-3 mechanism is beyond the scope of this document, some introductory material on basic concepts is included below for those unfamiliar with CB-3.

A distinguishing feature of any chemical mechanism is the manner in which organic reactivity is treated. Because the construction and use of a mechanism that includes all atmospheric species is virtually impossible, individual organic species must be combined, or lumped, into some sort of functional group, or groups. Thus, the discussion of any chemical mechanism must necessarily address the manner in which organic chemistry is represented in the mechanism. The concepts underlying the treatment of organic reactivity in CB-3 are discussed in Section 2.1 below.

As noted in Section 1.0, use of the CB-3 mechanism in a city-specific EKMA analysis is most easily accomplished with the OZIPM computer program. While the CB-3 mechanism has been designed in general form for use with any photochemical model, some adjustments are normally required to "fit" the mechanism to any particular computer code, and OZIPM is no exception. In addition, OZIPM requires a special input format for chemical mechanisms that warrants some explanation. These items are addressed in Section 2.2 below.

2.1 ORGANIC REACTIVITY

As described in Section 2.0, a characteristic that typically distinguishes chemical mechanisms is the manner in which organic compounds are represented in the mechanism. A number of approaches have been taken, but most have focused on lumping similar species into a single, identifiable molecular species that represents the chemistry of that particular class of compounds. For example, propylene might be used to represent the chemistry of all alkenes. The CB-3 mechanism is somewhat different in that the primary functional organic groups are based on various types of structural units (e.g., single-bonded carbon atoms) as opposed to molecular type (e.g., alkanes). As will be seen below, this kind of structuring results in some organic species being represented by more than one functional group.

In CB-3, seven functional groups are used to represent the role of organic species, each based on various types of carbon bonds:

(1) single-bonded carbon atoms, termed paraffins and represented by PAR;

(2) slowly reacting double bonds, almost exclusively ethylene and represented by ETH:

(3) relatively reactive double bonds, termed olefins and represented by OLE;

(4) reactive aromatic compounds, termed aromatics and represented by ARO;

(5) carbonyl compounds such as aldehydes and ketones, termed carbonyls, and represented by CARB;*

(6) highly photolytic, α -dicarbonyl compounds such as methyl glyoxal and biacetyl, termed dicarbonyls and represented by DCRB; and

(7) nonreactive compounds, represented by NR.

Of the seven groups listed above, users will be mostly concerned with Groups 1-5 and 7. DCRB compounds are primarily formed as products of chemical reaction. Hence, they are present, by and large, as a result of reactions occurring amongst the first five functional groups.

Just as important as the definition of the functional groups themselves is the manner in which individual organic species are apportioned to those groups. As noted above, a particular organic compound is assigned to a CB-3 group, or groups, on the basis of molecular structure. To illustrate the procedure, consider the propylene molecule which contains one single carbon-carbon bond and one double carbon-carbon bond (see Figure 2-1). In the CB-3 mechanism, the propylene molecule is represented by 1 paraffin and by 1 olefin. In essence, the molecule has been

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* In addition to aldehydes and ketones, olefins with internal double bonds are included in this group in order to eliminate intermediate species that have short lifetimes.

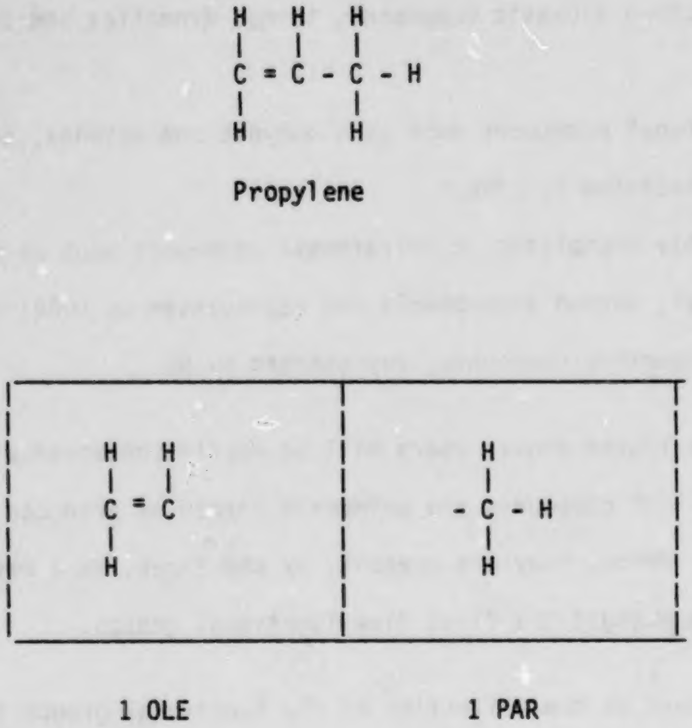
Propylene
1 OLE
1 PAR

Figure 2-1. Example of Carbon Bond Lumping Procedure

apportioned on the basis of the carbon-carbon bonds: the double-bond represented by OLE, and the one single bond by PAR. Similar classifications have been determined for scores of other compounds, and they provide the basis for establishing the overall reactivity of an urban mix.

In the propylene example discussed above, note that the number of carbon-atoms associated with PAR is one, while the number for OLE is two. A general principle underlying use of the carbon-bond mechanism is that the number of carbon atoms associated with any individual carbon-bond group is fixed. (Table 2-1 shows these characteristic carbon numbers for all six reactive carbon-bond functional groups.) By making use of the carbon numbers, concentrations of each CB-3 group can be determined from concentrations of individual organic species. To illustrate, consider the propylene example discussed above, and further assume that the concentration of propylene is 3 ppmC. Since propylene is represented in CB-3 by one PAR and by one OLE, the 3 ppmC total propylene concentration must be apportioned to these two carbon-bond groups. Of the three carbon atoms in a propylene molecule, one is PAR and two are OLE (see Figure 2-1). Thus, one-third of the carbon atoms can be thought of as PAR, and two-thirds as OLE. Since concentration is proportional to the number of carbon atoms, the concentrations of PAR and OLE in the CB-3 mechanism would be 1 ppmC and 2 ppmC, respectively.* This same concept can be extended to multicomponent mixtures as well. In such cases, concentrations of the individual organic

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* i.e., C_{PAR} = 1/3 x 3 ppmC and C_{OLE} = 2/3 x 3 ppmC

Table 2-1. Carbon Numbers for CB-3 Organic Species.

Carbon-Bond Group	Number of Carbon Atoms
Paraffins (PAR)	1
Ethylene (ETH)	2
Olefins (OLE)	2
Aromatics (ARO)	6
Carbonyls (CARB)	1
Dicarbonyls (DCRB)	3

species are first apportioned to their respective CB-3 group. The total concentration of any particular CB-3 group is then obtained by summing the contributions due to the individual organic species. This procedure will be more fully discussed in Chapter 3.

In using the CB-3 mechanism with the OZIPM program, absolute concentrations of the individual CB-3 groups are not directly input to the model. Rather, the total NMOC concentration is specified, and the fraction of carbon attributable to each CB-3 group is input. For example, assume that the total NMOC concentration is 2.0 ppmC, of which 1.4 ppmC is PAR (as determined by the procedure described in the preceding paragraph). Then the apportioning factor, or carbon fraction, for PAR would be 0.70, indicating that 70% of the total carbon is categorized as PAR. The CB-3 carbon fractions correspond conceptually to the DODGE mechanism apportioning factors of 25% propylene, 75% butane, and 5% added as aldehydes. The CB-3 fractions can be determined on a city-specific basis, or a special set of default values can be used. Both options will be discussed in Section 3.5.

2.2 USE OF CB-3 IN OZIPM

The general form of the CB-3 mechanism that is recommended by SAI for use with OZIPM is contained in Appendix A. The rationale and background information leading to this recommendation are contained in Reference 9. More extensive information on the evolution of the carbon bond mechanism in general can be found in References 7, 11, 12, 13, and 14.

As noted in Section 1.0, the OZIPM program is designed to accept any alternative mechanism, provided it is coded in a specified format. In addition to coding the chemical reactions and corresponding rate constants, all photolytic reactions and primary organic functional groups must be identified. Furthermore, those chemical species that undergo photolysis must be given special, pre-defined names. All of this information is input to OZIPM by means of the MECH option (see Reference 8 for details).

The specific inputs necessary to use CB-3 in OZIPM are contained in Appendix B (details of the format are contained in Reference 8 and summarized in Appendix B). It should be noted that to conform with OZIPM input requirements, the names of two species in the CB-3 mechanism listed in Appendix A must be changed: CARB to HCHO and DCRB to ALD2.* The species NR represents the nonreactive portion of organic compounds. Note that it is included as part of a "do-nothing" cycle, and does not affect the other reactions nor the amount of ozone formed. Finally, two additional reactions have been added to reflect the effect of tropospheric background on ozone formation (reactions 90 and 91 in Appendix B). The basis for these reactions will be discussed in Section 3.2.5.

The discussions in Section 2.1 and above have provided a general overview of the CB-3 mechanism and its relationship to the OZIPM program. In most instances, consideration of the details of the mechanism will not be required in any particular model application. The major concern in most applications is the determination of the total NMOC concentration, and then the specification of the carbon-bond fractions required to apportion the total carbon concentration to the individual carbon-bond groups (i.e., PAR, ETH, OLE, ARO, CARB, DCRB, and NR). The procedures for developing these and other model inputs for an EKMA application are the subject of the next chapter.

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* Even though the species labels HCHO and ALD2 are used in OZIPM, the CB-3 nomenclature of CARB and DCRB will be used throughout the text.

3.0 PROCEDURES FOR APPLYING EKMA/CB-3

Although the March 1981 guidelines deal explicitly with OZIPP and the DODGE mechanism, many of the concepts described in that document are relevant to the use of EKMA with other mechanisms as well. For example, selecting the cases to model and the manner in which isopleth diagrams are used to compute VOC emission reductions are unaffected by choice of chemical mechanism. Nevertheless, use of CB-3 with OZIPM does require some special considerations. This chapter will focus primarily upon these circumstances, but will also describe, in general terms, all other facets of conducting an EKMA modeling analysis. Again, the reader may refer to the March 1981 guidelines document for details regarding some aspects of the modeling methodology.

The ensuing discussion of using CB-3 with EKMA can perhaps be facilitated by a brief overview of the general modeling procedure. The OZIPM program is used to generate ozone isopleth diagrams that explicitly relate peak hourly ozone concentrations to initial (i.e., 8 a.m.) ambient levels of the ozone precursors NMOC and NO_x (see Figure 3-1). The diagrams are used with a measured peak ozone concentration and a city's NMOC/NO_x ratio to compute, on a percentage basis, the VOC emission reduction needed to lower the observed peak to the level of the standard. While isopleth diagrams are explicit functions of initial NMOC and NO_x, the positioning of the ozone isopleths on the diagram are also affected by model input variables that are related to meteorology, emissions occurring throughout the day, and pollutants transported from areas upwind of the

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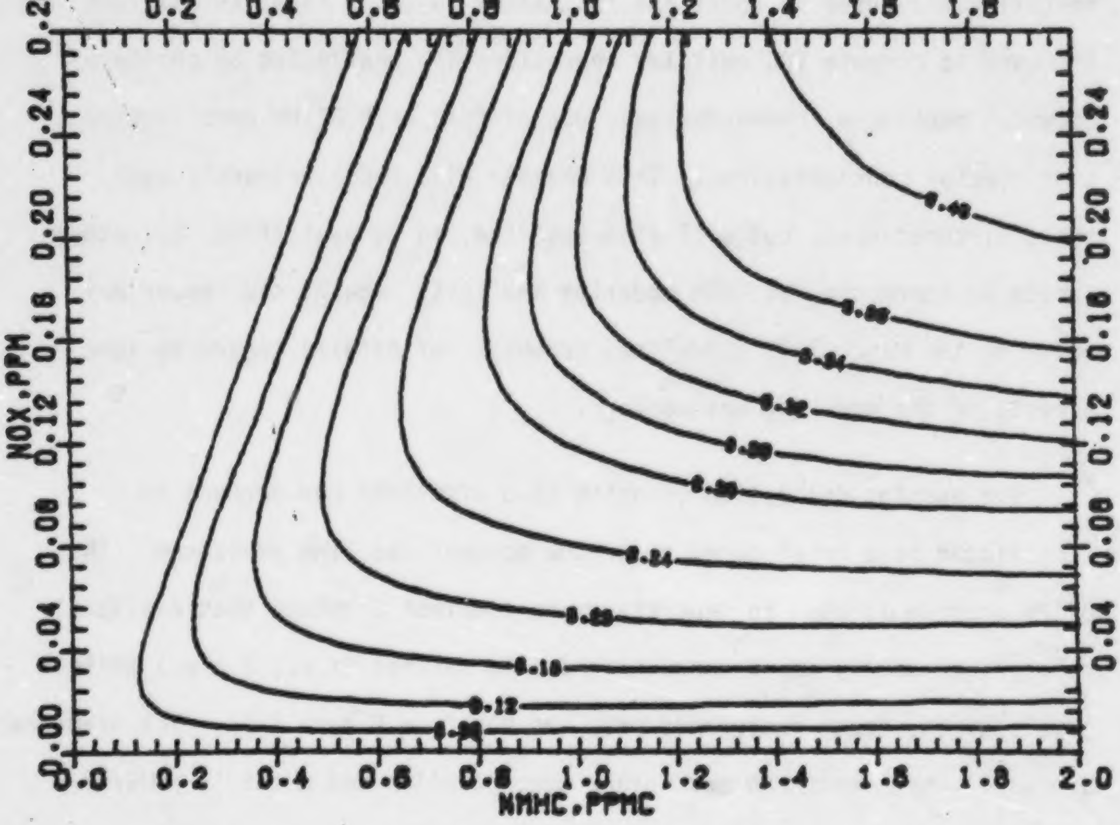

Figure 3-1. Example Ozone Isopleth Diagram.

city under review. Because these factors vary from day to day, the highest VOC emission reduction estimate will not necessarily correspond to the highest, observed ozone peak.[1,7] To account for this phenomenon, the modeling approach recommended in the March 1981 guidelines consisted of:

(1) modeling a number of high, observed ozone peak concentrations;

(2) computing the amount of VOC emission reduction needed to lower each peak to the level of the standard;

(3) selecting a final VOC emission reduction target that is consistent with the statistical form of the ozone standard.

Subsequent to the distribution of these recommendations, EPA issued supplemental guidance further recommending that predictions of peak ozone be compared to observed levels.[6] If the agreement between predictions and observations is found to be poor, review and possible adjustment to key model inputs are suggested prior to computing VOC emission reductions. While good agreement between predictions and observations does not completely insure accurate control estimates, successful prediction of observed ozone peaks does provide some confidence that the chemical and physical processes leading to ozone formation are being adequately simulated.

The modeling procedure described in the preceding paragraph can be divided into five basic steps:

(1) selecting the observed ozone peaks to model;

(2) formulating the model inputs;

(3) predicting peak ozone;

(4) computing VOC emission reductions; and

(5) selecting the overall VOC emission reduction target.

The remaining discussion is divided along these lines. For reference, only items 2, 3 and 4 above contain information that is new or significantly different from that found in the March 1981 guidelines. The other two topics are included for completeness, even though no major modifications have been made to the recommended approaches.

3.1 SELECTION OF MODELING CASES

As noted in Section 3.0, the highest VOC control estimate may not correspond to the highest observed ozone concentration. Further, the statistical form of the ozone NAAQS permits on average, one daily maximum, 1-hour average ozone concentration above 0.12 ppm per calendar year at each site.[15] Consideration of these two factors led to the recommendation that a number of observed peaks above 0.12 ppm be modeled. The VOC emission reduction target is then selected from these results in a manner that is consistent with the statistical form of the ozone NAAQS. For an EKMA/CB-3 analysis, the same procedure is recommended.

One additional issue could possibly arise when EKMA/CB-3 is used to replicate a modeling analysis conducted with EKMA/DODGE. In this situation, one may desire to use the original set of modeling results to reduce the modeling candidates for EKMA/CB-3 to some smaller subset. Given the complex nature of the nonlinear interactions embedded in the OZIPM model, the case with the highest VOC emission reduction may be different with EKMA/CB-3 than with EKMA/DODGE. As a result, the arbitrary elimination of any modeling case runs the risk of affecting the final VOC emission reduction target. Therefore, using EKMA/DODGE results to screen modeling cases from consideration with EKMA/CB-3 is not recommended.

Recommended Procedure: The recommended procedure for selecting the cases to be modeled is identical to that delineated on page 10 of the March 1981 guidelines document. Summarizing, the five (5) highest daily, maximum ozone concentrations at each site should be selected as candidates for modeling. Only ozone peaks that occur within or downwind of the urban area under review should be included. The five highest values should generally be chosen from the most recent three (3) years during which measurements were made at a site.

3.2 DEVELOPMENT OF MODEL INPUTS

As just described, the five highest, daily maximum ozone peaks at each site are selected for modeling. Two basic objectives of the modeling analysis are to predict the observed ozone peaks, and to compute the VOC emission reductions needed to lower each observed peak to the level of the ozone NAAQS. To best accomplish these objectives, the model inputs should be based on the atmospheric conditions associated with each observed peak. Thus, their derivation ought to be done on a case-by-case basis. In some instances, however, insufficient or inadequate data preclude such a determination, and appropriate approximations or defaults are needed. The major purpose of this section is to describe the methodologies recommended for deriving the model input values under both circumstances.

Table 3-1 summarizes the model input variables that require consideration, regardless of the intended purpose of the model simulation.

Table 3-1. OZIPM/CB-3 Model Inputs.

Model Input Variables	Section*	New Recommendations
> CB-3 mechanism	--	X
> Sunlight intensity	3.1.1	-
> Dilution	3.1.2	-
> Post-0800 emissions	3.1.5	-
> O_3 transport	3.1.3	-
> Precursor transport	3.1.4	X
> Initial NO_2/NO_x ratio	3.1.6	-
> Organic reactivity	3.1.6	X

* Refers to section numbers in the March 1981 guidelines (Reference 1).

Procedures for estimating many of these inputs have been discussed in the March 1981 guidelines, and the corresponding section numbers are shown for reference. With EKMA/CB-3, however, some supplemental guidelines for developing model inputs need to be provided, and are so noted in Table 3-1. While the discussion below will focus primarily on the new procedures, those that remain unchanged are briefly reviewed for completeness. Subsequent to that review, the recommendations for deriving the other model inputs are discussed in more depth.

Before discussing each of the model input variables, one final point should be added. The recommendations discussed below deal with model inputs that correspond to conditions associated with the observed ozone peak (i.e., so called base-case conditions). Some of these conditions might be expected to change in future years subsequent to the implementation of VOC control programs. Factoring these potential changes into the modeling analysis will be discussed in Section 3.4. Thus, the recommendations discussed below concerning the derivation of model input values will necessarily focus on data corresponding to emissions and atmospheric conditions associated with a particular ozone peak observed in the base case.

3.2 1 Model Inputs Without Significant Changes In Recommended Procedures

A number of model input variables are unaffected by the choice of chemical mechanism and, as a consequence, many of the recommendations contained in the March 1981 guidelines are also appropriate for CB-3. As might be expected, these variables primarily relate to the physical processes affecting ozone formation (as opposed to chemistry related variables). Examples include sunlight intensity, O_3 transport and dilution. While a detailed discussion of the procedures used to derive these inputs will not be repeated here, a brief review is included for background.

Light Intensity. The OZIPM program uses a city's latitude, longitude and time zone, and the day of the year being modeled to generate the appropriate diurnal pattern of photolytic reaction rates. While updates have been made to some of the photolytic rates, these have been incorporated in the CB-3 mechanism related inputs. Thus, no changes need be made for this set of model inputs.

Dilution. In the OZIPM model, dilution occurs as a result of the rise in atmospheric mixing height that typically occurs between early morning and mid-afternoon. The mixing height can be viewed as the top of a surface-based layer of air which is well-mixed due to mechanical and thermal turbulence. Specific inputs to OZIPM include the early morning mixing height, the maximum afternoon mixing height, the time that the mixing height rise begins, and the time at which the maximum mixing height is finally attained. In the March 1981 guidelines, procedures were provided for estimating the early morning mixing height and maximum afternoon mixing height from available radiosonde measurements. In the absence of such measurements, appropriate defaults were listed. Further, the OZIPM program will internally calculate the rate of rise in mixing height based upon a characteristic curve developed by Schere and Demerjian.[16,17] This is the procedure that is generally recommended for EKMA/CB-3 modeling analyses. However, OZIPM also contains an option whereby mixing heights can be specified for hourly intervals of the simulation period. This option can be used in place of the general recommendation whenever sufficient information is available to make such estimates.

Post 0800-Emissions. Post 0800-emissions refer to emissions occurring along the trajectory subsequent to the start of the model simulation. The actual model inputs are expressed as the fractions of initial NMOC and NO_x concentrations that should be added each hour to represent the effect of fresh precursor emissions. The March 1981 guidelines delineated the computational procedures that can be used to calculate emission fractions from the emissions data, the initial mixing height, and initial precursor concentrations. These same procedures are recommended for EKMA/CB-3 as well. (Note that the reactivity of the organic emissions will be addressed in Section 3.2.3.)

Initial NO_2/NO_x. The March 1981 guidelines recommended a default value of 0.25. Alternatively, the initial NO_2/NO_x ratio could be derived from early-morning, urban core measurements of NO and NO_2. No changes to these procedures are needed for application of EKMA/CB-3.

Ozone Transport. Ozone may be transported into a particular city either (1) within the surface-based mixed layer, or (2) above the early-morning mixed layer with downward mixing into the surface layer taking place as that layer increases in depth during the day. The March 1981 guidelines delineated procedures for deriving estimates of these quantities based on either direct measurement, indirect measurement or default estimate, and these are the procedures recommended for EKMA/CB-3 applications as well. However, some question has arisen as to the appropriateness of the assumption imbedded within OZIPM (and OZIPP) that the concentration of ozone aloft is constant throughout the simulation period.[4] Since little information is likely to be available to address this issue on a city-by-city basis, and since the effects of ozone aloft are likely to be most pronounced in mid-morning (i.e., the time at which the mixing height rises most rapidly), the assumption of a constant level aloft is still deemed most appropriate. However, if specific information is available to support a different approach, then appropriate adjustments could be made to the modeling procedure. It should be added that any such adjustments would require modifying the OZIPM computer code.

Summary of Recommended Procedures. The procedures recommended for formulating model input values for light intensity, dilution, post-0800 emissions, initial NO_2/NO_x, and ozone transport are identical to those delineated in the March 1981 guidelines. However, if sufficient city-specific information is available, then alternative approaches may be used to estimate a diurnal mixing height profile, or a diurnal profile in the concentration of ozone aloft.

3.2.2 CB-3 Mechanism

An introduction to the CB-3 mechanism was presented in Chapter 2, and the specific inputs that are needed to enter CB-3 into OZIPM have been included in Appendix B. Consequently, no more detailed discussion of the mechanism will be presented here. However, it should be added that the CB-3 mechanism recommended by SAI has undergone a wide range of tests, some of which have led to the selection of specific mechanism parameters. Further, the mechanism labeled as CB-3 in this document differs in several details from the mechanism identified as "CB-3" in References 7 and 24. In applying procedures described in this document, the mechanism described in Appendix B is the recommended version.

Recommended Procedure. The form of the CB-3 mechanism recommended for EKMA/CB-3 applications is contained in Appendix B. Pages B-2 through B-3 show the mechanism in the format that is required for input to OZIPM, with an accompanying explanation on page B-4.

3.2.3 Organic Reactivity

The fundamental concepts underlying the treatment of organic reactivity in the CB-3 mechanism were described in Section 2.1. As noted in that section, the organic reactivity input that is required by OZIPM consists of specifying a set of apportioning factors, or as they are more commonly termed, carbon-fractions. Specification of these fractions permits the OZIPM progam to apportion total NMOC concentration into the individual carbon groups - PAR, ETH, OLE, ARO, CARB, DCRB and NR.* (The apportioning procedure is carried out within the model for the NMOC concentrations that occur both initially and as a result of subsequent post-0800 emissions.) For comparison, the apportioning factors for the DODGE mechanism are 25%, 75% and 5% for propylene, n-butane and aldehydes, respectively.

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* Although DCRB is an organic carbon-bond group, initial concentrations and emissions of this group are very small compared to the others. Thus, the carbon fraction input for this group is normally zero.

Three basic approaches are possible for estimating the carbon-fractions. The recommended approach consists of using a set of default fractions that have been derived by SAI through analyses of available ambient organic species data, emissions inventory data, and review of pertinent, scientific experimental results.[7,9] The second, an alternative approach, requires the analysis by gas chromatography (GC) of individual organic species' concentrations in ambient air within the city under review. Typically, this approach requires a special field study. Another alternative approach involves the analysis of VOC emissions inventory data. In this case, the carbon-fractions are derived directly from the emissions data, provided that information is available on the quantity of species emitted by individual sources or source categories. Each of the three approaches is discussed in more detail below.

The recommended approach of using a default value rather than making a city-specific determination arises primarily as a consequence of two factors. First, the default values are estimated by SAI to be representative of typical urban reactivity based on ambient sampling results conducted in a number of locales.[7] While some city-to-city variations in organic composition are to be expected, the default recommendations should adequately represent most U.S. cities.[7,9] The second factor relates to the resource requirements associated with the two alternative approaches. Since they require either a special ambient sampling program or the compilation of emissions inventory data that is more detailed than normal, the resources needed to carry out these programs can be significant. Thus, use of the default values is normally recommended because of the expense associated with the more resource-intensive approaches.

Instead of using default values, carbon-fractions can be computed from GC analysis of ambient samples. References 18 and 19 discuss the monitoring aspects of GC analysis, and will not be repeated here. However, it should be noted that GC analysis is not an automated technique, and is most often done on a special study basis. Thus, a monitoring program of limited duration is the most pragmatic approach for developing the information needed to compute carbon fractions. While it is difficult to prescribe exactly the number of samples needed, enough should be analyzed to ensure that representative, average carbon-fractions can be computed. Since the carbon-fractions will be used to apportion initial concentrations and concentrations due to fresh emissions, the most appropriate sampling period is one prior to the onset of significant photochemical reaction. As with continuous total NMOC monitoring, sampling during the 6-9 a.m. time period within the area of maximum emission density (i.e., usually the center city) is generally recommended. Ambient samples for GC analysis can be collected either by integration over a period of one hour or more, or by grab sample in a few seconds. In general, the integrated method is preferable since the possibility of measuring short term fluctuations in species concentrations will be minimized.

The third basic approach involves the derivation of carbon-fractions from emissions inventory data. The technique makes use of a set of "split factors" that distributes total VOC emissions from a particular type of source, or source category, into individual organic species, which can then be aggregated according to the appropriate carbon bond groups.[20] The split factors can be determined on a source-by-source basis by source testing, or taken from literature sources such as Reference 21. Obviously, if a substantial number of source tests are undertaken, then this approach can be extremely resource intensive. In practice, the apportionment of total VOC emissions to carbon bond groups can be a rather intricate process, and should be conducted with the aid of a photochemical modeling specialist familiar with the carbon-bond mechanism. Publications that discuss the actual computational procedures include References 7, 9, 20, 21, 22, and 23. Because of the complexities involved, the details of the procedure will not be discussed in this document.

The three recommended approaches described in the preceding paragraphs lead to the derivation of a single set of carbon-fractions which apply to both the initial concentrations and the concentrations resulting from fresh emissions. Conceptually, the possibility exists for a separate set of carbon-fractions to be developed for the initial concentrations and the concentrations of the fresh emissions. Taking this concept one step further, carbon-fractions could even be developed for each hour of fresh emissions in order to account for potential spatial and temporal variations in the emissions of different species. (Obviously, the latter would require that an emissions inventory be of sufficient spatial and temporal resolution to identify such differences.) While these concepts are intuitively appealing from a modeling point of view, their inclusion in an EKMA/CB-3 modeling analysis is not recommended because the added sophistication does not justify the extra expense. If any of these last concepts are adopted, modifications to the OZIPM computer code will be required, since OZIPM is presently structured to handle only one set of carbon-fractions.

Regardless of the technique employed in their derivation, the carbon-fractions are used to apportion total concentrations of organic compounds which are based upon ambient measurements. Of the two organic compound monitoring techniques (i.e., continuous and GC), both rely on a flame ionization detector that is relatively inefficient in responding to many oxygenated compounds such as aldehydes and ketones (i.e., these techniques measure hydrocarbons only). SAI has estimated that, initially, total carbonyl compounds (i.e., those including aldehyde and ketones, as well as some surrogate carbonyls) are about 5% of total nonmethane hydrocarbon concentrations.[9] Only about 1% of the total carbon that is measured can be classified in the carbonyl group (i.e., surrogate carbonyls). The remainder of the carbonyls (i.e., 4% of the nonmethane hydrocarbons that are measured) is attributable to oxygenates that are not detected. Thus, the carbon-fractions should normally sum to 1.04 (or 104%).* If ambient measurements of aldehydes are available, a city-specific determination of the carbonyl fraction can be made. However, these measurements tend to be complex, using techniques that have not been standardized since they are mostly conducted by research groups. As a consequence, carrying out a special aldehyde monitoring program cannot be routinely recommended.

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* Note that this concept corresponds to the procedure used with the DODGE mechanism where total nonmethane hydrocarbon (NMHC) is split into 25% propylene and 75% butane, but 5% of the NMHC is added as aldehydes.

Whenever city-specific estimates are made by the techniques discussed above, special care must be taken to insure that the computed carbon-fractions represent a realistic distribution of NMOC species. SAI has developed ranges of probable carbon-fractions in order to ascertain whether the possibility of computational or measurement error has been introduced (Table 3-2). The use of any carbon distribution with an outlying carbon fraction(s) is not recommended with the version of CB-3 discussed in this document. The CB-3 mechanism has been tested over these ranges, and specific mechanism parameters have been chosen on this basis. Use of values outside this range will require a reformulation of the CB-3 mechanism. Thus, if a carbon-fraction falls outside of a probable range, the derivation of that value should be reviewed to insure that no errors have been made. In the event that no errors can be found, and the modeler is sure that use of a distribution with outlying carbon-fractions is warranted, the CB-3 mechanism should be modified. Obviously, consultation with a photochemical modeling specialist thoroughly familiar with the details of the CB-3 mechanism will be required to make any changes to the mechanism.

Table 3-2. Ranges of Urban NMOC Composition.*

Carbon-Bond Group**	Carbon-Fraction
PAR	0.50-0.70
ETH	0.02-0.11
OLE	0.02-0.07
ARO	0.10-0.40
CARB	0.03-0.10
NR	0.05-0.22

* From Reference 9

** DCRB assumed to be negligible

Recommended Procedure. The carbon-fractions recommended for use in an EKMA/CB-3 analysis are listed below:

PAR = .58
ETH = .04
OLE = .03
ARO = .19
CARB = .05
DCRB = .00
NR = .15

They can normally be used unless sufficient information is available to derive city-specific information by one of the methods discussed below.

Alternate Approach. If analyses of ambient air samples by gas chromatography are available for a particular city, the results can be used to derive carbon-fractions. The ambient samples should be taken in the high emission density area (normally the urban core) within the 6-9 a.m. Local Daylight Time (LDT) period during the ozone season. Integrated samples are generally preferable to instantaneous grab samples. It is desirable that enough samples be analyzed to provide a representative average. For supplemental information regarding monitoring aspects, the reader is referred to References 18 and 19, and for details on how carbon-fractions are computed from the sampling results, the reader is referred to Appendix C of this document.

Alternate Approach. If a detailed, speciated VOC emissions inventory is available, then those data may be used to compute carbon-fractions. For details of the procedures for compiling a speciated inventory and apportioning the emissions into carbon bond classes, the reader is referred to References 7, 9, 20, 21, 22, and 23. The aid of a photochemical modeling specialist familiar with the CB-3 mechanism will normally be required to conduct such an analysis.

Caveat: If either of the alternative approaches is used, the resultant carbon-fractions should fall within the ranges shown in Table 3-2. If they do not, it is strongly recommended that the data and computations be thoroughly checked to insure that no errors have been introduced. If the problem cannot be resolved, use of the default carbon fractions listed in the recommended procedure above is preferable. Because some mechanism rate constants were derived on the basis of the ranges given in Table 3-2, use of carbon fractions that fall outside of this range with the recommended form of the CB-3 mechanism may lead to unrealistic results, and is not recommended.

3.2.4 Precursor Transport

The guidelines for applying EKMA/DODGE contained a recommendation that precursor transport (both in the surface layer and aloft) not normally be considered. Sensitivity tests conducted with EKMA/DODGE revealed that VOC control estimates are not substantially altered by typical levels of precursor transport.[1] Also, the measurements that are typically required to characterize the levels of precursor transport can be expensive, difficult to make and generally require special field studies. Given these problems, the routine consideration of precursor transport in EKMA/DODGE is difficult to justify. (Nevertheless, the 1981 March guidelines do provide for its consideration for the benefit of those who desire to account explicitly for its effect.) Sensitivity tests conducted with EKMA/CB-3, however, suggest that these same recommendations are not always appropriate for EKMA/CB-3 analyses. Thus, some supplemental guidance in this area is needed.

First, consider the role of NO_x transport. Sensitivity tests conducted with EKMA/DODGE have revealed that control estimates are not critically affected by typical levels of NO_x transport. The same general finding holds true for EKMA/CB-3 as well. Thus, routine consideration of NO_x transport is not generally recommended, but the procedures outlined in the March 1981 guidelines can be used to incorporate it in an EKMA/CB-3 analysis if so desired. As noted in the 1981 guidelines, measurements that may not be routinely performed are required to estimate NO_x transport levels. The reader is referred to Appendix B of the 1981 guidelines for additional details.

As noted above, EKMA/DODGE exhibits relatively little sensitivity to typical organic precursor levels that may be transported into a city from upwind areas. Such is not always the case with EKMA/CB-3, however. As a consequence, dealing with precursor transport in an EKMA/CB-3 analysis warrants special consideration. For analysis purposes, it is convenient to divide the precursor transport into two components: (1) naturally occurring background, and (2) "manmade transport" that is generated by significant, upwind source areas.[9] Natural background represents a ubiquitous component of ambient organic compounds that is irreducible (i.e., the background organics will likely be unaffected by the implementation of VOC control programs). On the other hand, "manmade transport" levels will depend on a city's location relative to other source areas and the meteorological patterns that affect transport between source areas. Consequently, one would expect the manmade transport levels to vary from city-to-city, and that future levels might be reduced as a result of the implementation of VOC control programs in upwind source areas. Thus, the approaches for dealing with each are necessarily different, and the discussion below will be divided along those lines.

Natural Background. SAI has investigated the role of background organics vis-a-vis photochemical modeling with the CB-3 mechanism.[9,24] In their studies, SAI has subdivided naturally occurring background into two components: (1) a tropospheric component that occurs on a global scale, and (2) a continental component that is associated with the surface-based mixed layer over the continental portion of the

United States. For purposes of the ensuing discussion of these two types of background, reactivity is defined as the rate at which hydroxyl radicals react with atmospheric organic compounds to form peroxyl radicals, e.g.,

$$OH + HC \dashrightarrow RO_2\cdot \qquad (3\text{-}1)$$

The peroxyl radicals are responsible for converting NO to NO_2 in the sequence of reactions that eventually lead to significant ozone formation. High concentrations of slowly reacting species can have the same reactivity as low concentrations of highly reactive compounds. True background mixtures will usually react slowly, and be relatively stable in terms of concentration. Species that react more rapidly are normally associated with fresh emissions.

As noted above, tropospheric background is intended to represent background reactivity on a global scale. It is based on measurements of light hydrocarbons and CO taken over the eastern Pacific Ocean. The reactivity of this mixture has been calculated, and photochemical mechanisms used to estimate the equilibrium concentration of other compounds, such as carbonyls.[9] It should be added that some of the compounds that make up the tropospheric background are normally considered unreactive because of their relatively slow rate of reaction with hydroxyl radicals (examples include methane and ethane). Nevertheless, the sum effect of their presence should be accounted for in an EKMA/CB-3 analysis. However, because the concentrations of the tropospheric background compounds do not vary substantially, their effect can be accounted for in the CB-3 mechanism directly. SAI has recommended that the tropospheric component be included in the chemical mechanism by means of the following two reactions:*

$$OH \longrightarrow MEO2 \qquad k = 28\ min^{-1} \qquad (3\text{-}2)$$

$$OH \longrightarrow HO2 \qquad k = 88\ min^{-1} \qquad (3\text{-}3)$$

As can be seen in Appendix B of this document, these two reactions have been included as reactions 90 and 91 in the recommended form of the CB-3 mechanism.

In addition to the natural tropospheric background just discussed, boundary layers over land masses receive a variety of organic emissions that result in a continental background contribution over and above that of the tropospheric component. These emissions occur as a result of various biogenic, geogenic and anthropogenic processes. In general, distinctions among these sources cannot be made from ambient measurements alone because the composition of organics emitted from these sources exhibit considerable overlap, and because the composition of some emissions, especially those from biogenic sources, has not been well characterized. It should be added that the measurements referred to here have been taken in relatively "clean air" within the continental United States. Thus, this continental background represents an irreducible component of ambient organic compounds, although a portion may actually be the result of anthropogenic activity.

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* Source: Reference 9

The continental background concentrations recommended by EPA are, in turn, based on recommendations by SAI which consider measurements taken in rural areas, and represent continental "clean air" conditions. In their review of the data, SAI found that the concentrations of organic species attributable to continental background gradually decreased with height until the tropospheric background was approached at heights typically above the early morning mixed layer. SAI recommends that the total mass loading of the continental background be represented by a single concentration that represents the average level within the surface-based mixed layer. To account for variations in the height of this layer, SAI further recommends that the average concentration should be inversely proportional to mixing height. For EKMA/CB-3 applications, this recommendation can be implemented by deriving the continental background concentration relative to the initial mixing height. The estimated continental background concentration should then be assumed to prevail throughout the surface layer in the model. For an initial mixing height of 250 meters, SAI recommends that the concentrations of carbon-bond species shown in Table 3-3 be added to the urban initial NMOC concentration.[9] If the mixing height is greater than 250 meters, then the total background NMOC concentration should be reduced by a factor that is proportional to the ratio of 250 meters to the higher initial mixing height. For example, if the initial mixing height were 500 meters, the total NMOC concentration of .038 ppmC (Table 3-3) would be reduced by a factor of 1/2 (i.e., $\frac{\text{250 meters}}{\text{500 meters}} = 1/2$). Thus, continental background can be viewed as the result of continuous

Table 3-3. Recommended Continental Background.

Species	Recommended Concentration, ppmC	Computed Carbon Fraction
PAR	0.020	.53
ETH	0.002	.05
OLE	0.001	.03
ARO	0.005	.13
CARB	0.010	.26
DCRB	0.000	.00
NR	0.000	.00
TOTAL	0.038*	1.00

* The 0.038 ppmC total is relative to a 250 meter initial mixing height. For other initial mixing heights, the total concentration should be adjusted by the following equation (with the same carbon fraction used):

$$C_{BKG} = (0.038\ \text{ppmC})\ \frac{(250\ \text{meters})}{H_o}$$

where

C_{BKG} = adjusted background concentration, ppmC

H_o = initial mixing height, meters

areawide emissions producing ambient concentrations that are proportional to the depth of the mixed layer.

Manmade Transport. The tropospheric and continental backgrounds discussed above represent a ubiquitous and irreducible component of ambient organic concentrations.* As noted above, the possibility exists that organic precursors generated by upwind source areas may be transported into a city. In the discussions that follow, the manmade component is to be viewed as the contribution of organic precursors over and above those occurring naturally.

In the context of the OZIPM model, manmade transport could occur in the surface layer, aloft (i.e., above the early morning mixed layer), or both. Of particular importance with EKMA/CB-3 is the concentration of organics aloft. To illustrate its importance, a series of sensitivity tests were conducted with EKMA/CB-3 in an effort to quantify the potential effect, and the results are summarized in Table 3-4. Predictions of peak ozone in the base case are not substantially affected by the assumed levels aloft, but VOC control estimates are relatively sensitive to the assumed levels.** Further, measurements taken aloft in a number of cities encompass the levels used in these sensitivity tests.[26,27]

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* Irreducible in this context means that the background organics will likely be unaffected by the implementation of control programs.

** It should be added that this same sensitivity may not be exhibited under all conditions. Nevertheless, the model inputs chosen for these tests are similar to those used for many urban areas.

Table 3-4. EKMA/CB-3 Sensitivity to Precursor Concentrations Aloft.

Precursor concentration aloft,* ppmC	0.000	0.010	0.020	0.030	0.040	0.050
Prediction of peak ozone, ppm	0.223	0.223	0.227	0.229	0.231	.232
VOC control estimate,† %	39	43	43	46	48	51

* See page 43 for the assumed composition of precursors aloft

† All estimates made assuming a 40% reduction in levels aloft in future years

These measurements indicate that levels aloft vary from city to city. A comprehensive review of NMOC measurements aloft is underway, and this review may enable recommendations concerning default estimates to be made in the future. The only alternative approach that can currently be recommended is to measure organic precursors aloft on a city by city basis. Unfortunately, such measurements are difficult to make, and very resource intensive. Nevertheless, they appear to be necessary to characterize typical levels aloft.

Appendix B of the March 1981 guidelines describes the measurements that are needed to estimate concentrations of precursors aloft being transported into an urban area. However, it is more than likely that measurements will not be available for some of the days that need to be modeled. In these cases, the March 1981 guidelines recommended that median concentrations from all available measurements be used. This procedure can be enhanced by associating particular measurements with prevailing wind direction and possibly atmospheric conditions associated with ozone episode conditions. For example, a particular city could be located such that a heavily populated and/or industrialized area lay to the south, but predominantly rural areas extend to the west. Early morning organic measurements taken upwind or aloft would provide some indication of the manmade transport. However, the manmade transport contribution would be expected to be much greater for a windflow out of the south rather than one from the west. Thus, the available measurements could be grouped according to wind direction, in order to estimate manmade transport levels on other days with similar flow patterns.* The measurements could be further stratified according to ozone episode conditions (i.e., days with high ozone levels versus those with low levels). Again, median values for each category could be used as estimates for those cases in which day specific measurements are unavailable.

A second factor to consider with regard to these types of measurements is the heights at which they are taken. The results of studies conducted previously to characterize organics aloft suggest that concentrations vary with altitude.[27] Any measurement program that is undertaken should attempt to characterize the concentrations of organics within the layer that will be entrained into the afternoon mixed layer as a result of the increase in mixing height later in the day.** For example, if the mixed layer normally grows from 250 meters to a height of 1500 meters by the afternoon, then the measurements should be taken at varying heights between 250 meters and 1500 meters. The OZIPM model inputs should then be based on the average concentrations found in the 250 meter to 1500 meter layer. If measurements are available at only one height, then these measurements alone will have to suffice.

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* Ideally, wind measurements should be taken aloft at altitudes below the maximum afternoon mixing height. If only surface wind measurements are available, relationships between surface wind and wind aloft on days with NMOC measurements aloft should be used in categorizing days on which surface wind measurements alone are available.

** Note that the measurements should be taken in the early morning, before the growth in the mixed layer begins, in order to determine the concentrations that will be entrained later in the day.

Given that measurements of organic compounds aloft are available, some additional adjustments should be made in order to estimate the final OZIPM model inputs. First, the tropospheric background embedded in the CB-3 mechanism accounts (at least partially) for unreactive compounds that may exist aloft, and for about 0.010 ppmC of all reactive compounds. Thus, if concentrations of individual species are available (e.g., by GC analysis), then only the reactive constituents need be considered when estimating total concentrations of organics aloft. (Table C-1 of Appendix C identifies those compounds classified as unreactive.) Further, the total concentration aloft that is derived from the measurements should be reduced by 0.010 ppmC to avoid "double-counting" the reactive, tropospheric background component. Finally, if the measurements aloft are made by Flame Ionization Detector (FID), oxygenated compounds (i.e., carbonyls) will not be detected. While precise estimates are difficult, SAI's study of photochemical modeling results suggest that roughly 15% of nonmethane hydrocarbons transported into an urban area can be classified as carbonyls.[9] In the absence of specific measurements of oxygenated compounds, the 15% value is recommended as a default.

To illustrate the recommendations described above, assume that nonmethane hydrocarbon measurements, including only reactive compounds, totaled 0.040 ppmC. First, the 0.010 ppmC reactive tropospheric component would be subtracted from this level, and then the resultant increased by 15% to account for unmeasured carbonyls (i.e., [0.040-0.010] x 1.15 = 0.035 ppmC). Thus, 0.035 ppmC would be the OZIPM estimate for organic compounds aloft. However, the composition of the levels aloft must also be specified. If measurements of individual species are available, then the average composition derived from the measurement concentrations can be used. If such measurements are not available, then the following default carbon-fractions are recommended:

PAR = 0.61
ETH = 0.06
OLE = 0.03
ARO = 0.15
CARB = 0.15
DCRB = 0.00
NR = 0.00

The default was calculated from the fractions used for the continental background (Table 3-2), but adjusted to reflect only a 15% carbonyl composition. This default composition is consistent with SAI's estimate for manmade transport, although slightly lower in carbonyls and ethylene, and slightly higher in aromatics and paraffins.[9]

Recommended Procedure. (1) To account for a global, tropospheric background of organic compounds, two reactions have been included in the recommended form of the chemical mechanism. No additional input is required of the user. (2) A specified set of concentrations have been recommended to account for a continental background (Table 3-3). These backgrounds represent irreducible components of atmospheric organic compounds, and are recommended for all EKMA/CB-3 analyses. The continental background concentration should be considered in the surface layer of the model only. (3) While measurements for manmade transport are complex and resource-intensive, the sensitivity of EKMA/CB-3 control estimates to this factor suggests its explicit consideration. Such measurements should be taken above the mixed layer in the early morning at varying heights in order to establish the average concentration in the layer that will be entrained as the mixing height grows to its maximum. Since tropospheric background accounts for some of the species concentrations measured aloft, only the reactive components should be considered and the measurements should be reduced by 0.010 ppmC to account for the reactive tropospheric background component. If measurements of oxygenated compounds are not available, then the resultant concentration should be increased by 15%

(all CARB) to account for these compounds. The composition of the organics aloft can be determined from the measurements by the procedures described in Appendix C. Alternatively, the composition listed above can be used. In the event NMOC data aloft do not exist for certain of the days to be modeled, wind data should be examined so as to categorize each day with measurements. If sufficient information exists, the days with measurements should be further categorized by ozone episode conditions. Then, for those days without measurements, the median NMOC level of a particular category can be used as an estimate for a day that corresponds to that category.

3.3 PREDICTING PEAK OZONE

In one study, it was found that EKMA could yield a lower control estimate for a case when peak ozone is underpredicted as compared to one in which peak ozone is more accurately predicted.[4] In extreme cases of underprediction, a solution may not be possible with EKMA. In a similar fashion, a large overprediction could lead to a control estimate that is higher than that obtained when good agreement is found. As part of the supplemental EKMA guidance issued in December of 1981, EPA addressed this problem by recommending that predictions of peak ozone be made on a routine basis, and appropriate adjustments or compensations be made if poor agreement is found.[6] In this section, the procedures for making the predictions, comparing them with observations and making appropriate adjustments are described. It should be added that the discussion below is not peculiar to the CB-3 mechanism, but applies to use of any mechanism with the EKMA technique.

3.3.1 Procedures for Making Ozone Predictions

In Section 3.2, most of the OZIPM model inputs that are needed either to predict peak ozone or to estimate VOC emission reductions were discussed. In order to make predictions of peak ozone, one additional set of model input variables is needed: the concentrations of NMOC and NO_x that are representative of the initial (i.e., 8 a.m.), urban core levels. These model inputs are the most critical for making predictions, and should be estimated on a case-by-case basis. Because of the model sensitivity to these inputs, use of mean or median values compiled from measurements taken across a number of days may lead to erroneous results. Thus, day-specific measurements should normally be used to make these estimates.

As for estimating the initial concentrations, the recommended procedure is to make use of ambient NMOC and NO_x measurements routinely taken in the urban core. The initial concentrations are intended to represent the NMOC and NO_x that is initially present within the mixed layer at the start of the model simulation (i.e., 8 a.m.). While several approaches could be taken, the recommended method is to use the 6-9 a.m. average concentration measured by collocated NMOC and NO_x monitors within the urban core. If more than one pair of measurements are available from a set of such monitors, then the 6-9 a.m. average concentration at each monitor should be averaged to obtain an overall, urban average NMOC and NO_x concentration. Algebraically, the above procedure can be expressed as follows:

$$(C_{NMOC})_0 = \frac{\sum_{i=1}^{N} [(C_{NMOC})_{6-9}]_i}{N} \qquad (3\text{-}4a)$$

and

$$(C_{NOx})_o = \frac{\sum_{i=1}^{N} [(C_{NOX})_{6-9}]_i}{N} \qquad (3\text{-}4b)$$

where

$(C_{NMOC})_o$, $(C_{NOx})_o$ = initial concentrations of NMOC and NO_x (in units of ppmC and ppm, respectively) input to OZIPM simulation

$[(C_{NMOC})_{6-9}]_i$, $[(C_{NOx})_{6-9}]_i$ = the 6-9 a.m. average concentrations of NMOC and NO_x (in units of ppmC and ppm, respectively) taken in the urban core (or high emission density area) at site i

N = total number of collocated monitors for which day-specific NMOC and NO_x measurements are available.

As noted above, the initial NMOC and NO_x concentrations are derived from day-specific measurements of NMOC and NO_x. In some instances, an NMOC measurement may not be available for the day being modeled. In such a case, the initial NMOC concentration can be approximated by making use of the median NMOC/NO_x ratio and a day-specific measurement of NO_x alone, provided it is available. The initial NMOC concentration for use with the OZIPM simulation can be computed as the product of the median NMOC/NO_x ratio and initial NO_x concentration, or

$$(C_{NMOC})_o = (C_{NOx})_o \, (NMOC/NO_x) \qquad (3\text{-}5)$$

where

$(C_{NMOC})_o$ = the initial NMOC concentration for the OZIPM simulation, ppmC

$(C_{NOx})_o$ = the initial NO_x concentration calculated by equation 3-4b, ppmC

($NMOC/NO_x$) = the median $NMOC/NO_x$ ratio as derived according to the procedures outlined in Section 3.4

It should be emphasized that this approach is an approximation, and the one described in the preceding paragraph is preferable.

With the estimates of initial NMOC and NO_x, and the corresponding day-specific inputs listed in Table 3-1, the CALCULATE option of OZIPM may be used to perform a single model simulation. An example simulation will be described in Section 4.2, and additional information is contained in Reference 2. Thus, no additional discussion will be included here.

Recommended Procedure. The CALCULATE option of the OZIPM program should be used to predict peak ozone for comparison with the observed peak. The model inputs discussed in Section 3.2 should be used, with initial concentrations that have been derived according to equations 3-4a and 3-4b, using data that are specific to the day being modeled. In the event that day-specific NMOC measurements are unavailable, the initial NMOC concentration can be approximated by means of equation 3-5, with the recognition that some uncertainty may be introduced in the analysis. If day-specific measurements of NMOC and NO_x are not available, predictions of peak ozone cannot be made. In this case, computation of VOC control estimates are recommended, but without the requirement of reasonable agreement between prediction and observation.

3.3.2 Comparisons of Predictions With Observations

The principal output of concern obtained with a CALCULATE simulation is the predicted ozone. By numerically integrating the differential equations describing ozone formation processes (i.e., chemical reaction, emissions, dilution, etc.), instantaneous concentrations of ozone are computed throughout the simulation period. (For example output see Section 4.2). From this computed profile of instantaneous ozone concentrations, the OZIPM program calculates the maximum 1-hour average concentration occurring during the model simulation. It is this maximum 1-hour average concentration that is generally recommended for comparison with the observed ozone peak. The model performance measure that is generally recommended is the relative deviation of the prediction from the observation, or

$$\mathrm{DEV} = \frac{C_p - C_o}{C_o} \times 100 \qquad (3\text{-}6)$$

where

DEV = deviation of the model prediction from the observation, percent

C_p = maximum 1-hour average predicted peak ozone, ppm

C_o = observed peak ozone, ppm

If the relative deviation is found to be within ± 30%, then agreement between the prediction and the observed peak is judged to be sufficient to proceed with control estimate calculations. If the model underpredicts by more than 30% (i.e., DEV < - 30%) or overpredicts by more than 30% (i.e., DEV > + 30%), then review of, and possible adjustment to, key model inputs according to the discussion of Section 3.3.3 below is warranted. It should be noted that the observed ozone peak (not the predicted) is recommended for subsequent control calculations.

Recommended Procedure. The relative deviation of the model prediction from the observed peak should be computed according to equation 3-6 above. The model predicted peak to be used in this computation is the maximum 1-hour average ozone concentration calculated by the OZIPM program. If the computed deviation is within + 30%, then the model results are sufficiently accurate for control estimate calculations. If the deviation is outside the ± 30% envelope, then the procedures discussed in Section 3.3.3 should be applied in an attempt to improve the simulation results.

3.3.3 Review and Adjustment to Model Inputs

If inadequate agreement between a model prediction and an observed peak is found, review of the model inputs is recommended. The objective of this review is to investigate whether some modifications to key model inputs can be made in order to improve the model predictions. This review should focus on those model inputs that most critically affect predictions of peak ozone. Of most importance are the initial NMOC and NO_x concentrations, dilution and post-0800 emissions. Adjustment of these inputs, within the uncertainties associated with their development, is warranted if improvements in model predictions can be made. Obviously, any errors that may have been made in their derivation should be corrected as well.

While specific recommendations in trouble-shooting poor model performance are difficult to make, some general guidelines can be made depending on the nature of the problem, be it an underprediction or an overprediction. Consider the case of underprediction first. Causes of underprediction could result from initial concentrations being too low or dilution being too great (i.e., the initial mixing height being too low, the maximum afternoon mixing height being too great, or both). These inputs should be reviewed to see if any errors have been made in their estimation. If some uncertainty exists with regard to the data from which they were derived, then the inputs can be adjusted within that range. For example, assume that an initial NMOC concentration had been derived from 6-9 a.m. measurements taken at three monitoring sites. However, the 6-9 a.m. concentration at one site (say site A) deviated substantially from the concentrations measured at the other two sites (say sites B and C). Then, improved agreement between model predicted and observed ozone might be found if the initial NMOC concentration for the day in question was derived solely from the measurements taken at the two sites in agreement (i.e., sites A and B). Note that, if the initial concentrations and/or the initial mixing heights are adjusted, corresponding modifications should be made to the post-0800 emissions as well. In addition, alterations to the initial mixing height would require changes to the assumed continental background concentrations as discussed on pages 36-37. Another possible cause for underprediction could lie in the organic reactivity inputs that are used with the CB-3 mechanism. The values that are being used should be checked to insure that they lie within the recommended ranges listed in Table 3-2. However, day-specific adjustments are not recommended.

Guidelines for correcting a problem of overprediction are similar in concept to those for underprediction. For example, initial concentrations could be too high, and/or dilution too low. Again, these inputs might be adjusted within the range of reasonable uncertainty. As an example, assume that mixing height data were computed using two sets of radiosonde measurements and the averages used as model inputs. In a case of overprediction, then, the largest of the two afternoon maximum mixing heights might be input rather than the average. In addition to these types of adjustments, it is recommended that the ozone predicted at the time of the observed peak also be reviewed.* A situation could exist whereby the observed peak occurs relatively early in the simulation period, and the model predicted maximum 1-hour average ozone occurs late in the simulation. If the ozone level predicted at the time of the observed peak agrees to within ± 30% of the observed level, then that result indicates adequate agreement for control calculation purposes, and no further adjustments need be made.

As noted above, two key model inputs that substantially affect model predictions of peak ozone include the initial NMOC and NO_x concentrations, and initial mixing height. The possibility exists that mass balance techniques could be used to evaluate the appropriateness of a particular set of initial concentrations and an initial mixing height. For example, one could test by means of a simplified box model whether or not a city's emissions are sufficient to generate the measured initial concentrations within a mixed layer corresponding to the postulated initial mixing height. While such an approach is intuitively appealing, such calculations may not be able to account properly for ventilation, and for advection of pollutants from source areas nearby the precursor monitors. Nevertheless, it does provide one means of assessing the reasonableness of the postulated model inputs. Again, it should be added that any adjustment to the initial concentrations and/or initial mixing height will affect the post-0800 emission fractions, necessitating their recomputation.

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* The predicted, hourly average ozone concentration at the time of the observed ozone peak can be approximated from the instantaneous predictions by averaging the instantaneous predictions corresponding to the hours bracketing the time of the observed peak. For example, if the observed peak occurred between 1 and 2 p.m., then the instantaneous predictions at 1 p.m. and 2 p.m. could be averaged. Alternatively, more rigorous integration techniques could be used to compute the integrated, hourly average.

Recommended Procedure. Model inputs can be manipulated within reasonable ranges to determine if improvement can be made in the agreement between the model predicted peak ozone and the observed peak. Specifically, the key model inputs are initial NMOC and NO_x concentrations, mixing heights and post-0800 emissions. In addition, CB-3 organic reactivity inputs should be checked to insure that they conform to the recommended ranges listed in Table 3-2, but day-specific adjustments are not recommended. While the other model inputs can be reviewed and adjustments made where appropriate, their relative importance vis-a-vis predicting peak ozone is not deemed as critical as the aforementioned variables. Finally, model inputs should only be adjusted within the range of reasonable uncertainty, and not just selected such that good agreement between the model prediction and observed peak is obtained. Finally, if acceptable agreement cannot be found, control estimates should still be made and the procedures discussed in Section 3.5 applied.

3.4 COMPUTING VOC EMISSION REDUCTIONS

The procedures for computing VOC emission reductions from ozone isopleth diagrams have been described in Reference 1, among others. In the first step, the OZIPM program is used to generate a base-case isopleth diagram. This is normally accomplished by using the same model inputs that are used to make predictions of peak ozone, except that the CALCULATE option is replaced with the ISOPLETH option. A base, or starting, point is then located on that diagram using two pieces of empirical data - a city's prevailing $NMOC/NO_x$ ratio and the observed ozone peak for the case being modeled. If changes in VOC and/or NO_x emissions are the only changes projected, then the base-case diagram can be used by itself to make the necessary computations. However, if changes in factors such as ozone transport or precursor transport are projected to take place concurrently with changes in precursor emissions, then a second, future case diagram must be generated. This section will focus on developing the empirical data that are needed, generating the base case diagram, and factors to consider in the generation of a future case diagram. For details of the computational procedures that are involved in making VOC emission reduction estimates, the reader is referred to Reference 1, the March 1981 guidelines.

3.4.1 Derivation of Empirical Data

As noted above, two pieces of empirical data are used to establish a starting point on the base case isopleth diagram. The first is simply the ozone peak that was measured on the day being modeled. The second is the $NMOC/NO_x$ ratio prevailing in the city under review. The procedures that are recommended for estimating these values for an EKMA/CB-3 application are identical to those delineated in the March 1981 guidelines.[1] They are briefly summarized below.

Recommended Procedure. Details of the recommended procedures for estimating the ozone peak and a city's prevailing $NMOC/NO_x$ ratio that should be used to establish the starting point on a base-case isopleth diagram are contained on pages 39 through 43 of the March 1981 guidelines.[1] In summary, the ozone peak is the maximum 1-hour average level measured at the site/day under review. The $NMOC/NO_x$ ratio is determined from 6-9 a.m. measurements taken at collocated monitoring sites within the urban or high emission density area. If measurements are taken at only one monitoring site, then the ratio to be used in EKMA calculations should be the median of the ratios found on all days that are being modeled for which accompanying NMOC and NO_x data are available. Use of a day-specific ratio is recommended only when data are available at more than one monitoring site, and the individual ratios at each site do not differ by more than ± 30% from the average ratio.

3.4.2 Generating Base Case Diagrams

Generation of a base case diagram with OZIPM is carried out by using the model inputs described in Section 3.3 and the ISOPLETH option. The only additional inputs associated with the ISOPELTH option are those controlling the NMOC and NO_x scales of the diagram. As with EKMA/DODGE, these values should be chosen such that the starting point is located towards the right-hand portion of the isopleth diagram in order to facilitate accurate VOC emission reduction calculations. This topic is addressed in greater detail in the OZIPP User's Manual, Reference 2.

As was noted in Section 3.3.3, some situations may arise in which predicted peak ozone values agree more closely with observed levels if the predicted value corresponds to the time of the observed peak, rather than to the maximum value occurring during the simulation. Such a factor might suggest that, for control calculation purposes, the length of the simulation should be shortened to correspond to the time needed to reach the observed peak. In general, full 10-hour simulations are recommended for these cases, but the option exists to shorten the simulation using the OZIPM TIME option (see Reference 8). However, modeling analyses suggest that ozone peaks are likely to occur later in the day as VOC controls are implemented.[25] As a consequence, when a simulation length is shortened for the generation of the base case diagram, a future case diagram generated with a full 10-hour simulation length is recommended.

This procedure will insure that the VOC control calculations will properly account for the lengthening of the time to peak ozone associated with the implementation of a VOC control program.

Recommended Procedure. Standard techniques for generating base case diagrams are recommended. An example problem is discussed in Section 4.3. One possible option that can be invoked is one of shortening the simulation length to correspond to the time of the observed peak. The approach would normally be taken only if the ozone predicted at the time of the observed peak agreed much more closely with the observation than the simulation maximum. In any event, a future case diagram using a full 10-hour simulation period is recommended.

3.4.3 Generating Future Case Diagrams

As explained above, the generation of a future case diagram is only necessary if changes in factors other than precursor emissions are projected to take place. Such factors could include projected changes in ozone transport, precursor transport, and/or a possible shift in organic reactivity. (Note that only one future base diagram is needed to incorporate all of these changes.) This section will focus exclusively on how these changes are estimated. The procedures for generating the diagrams are identical to those used for the base case diagram, with only the relevant model inputs changed. For additional background material, the reader is referred to pages 49-61 of the March 1981 guidelines document.[1]

The March 1981 guidelines provided procedures for projecting changes in ozone and precursor transport due to the implementation of VOC control programs upwind of a city. Basically, these recommendations remain intact. With regard to ozone transport, the diagram on page 54 of the March 1981 guidelines document can be used to project the changes in ozone transport. Likewise, the guidelines document recommended that NMOC precursor transport levels could be reduced by 40% if a city was impacted by nonattainment areas upwind, 20% if otherwise. Again, these same recommendations hold with the added caveat that only "manmade" NMOC transported levels should be reduced (see Section 3.2.5). In addition, no adequate procedure currently exists to project how the composition of the manmade, transported organic compounds might change in the future. As a consequence, the same composition of manmade and background organics is recommended for both base and future cases.

The possibility exists that, as VOC emission controls are implemented, a shift in a city's organic reactivity could take place. This could occur if particular NMOC species are controlled to a greater or lesser extent than others, and/or if the control program itself caused a shift in the emissions of particular species. Conceptually, this possiblity can be accommodated in the modeling analysis by generating a future case diagram using the projected change in NMOC composition (i.e., a set of carbon-fractions representing the future case). Because of the great uncertainties associated with making such projections, attempting to account for reactivity shifts is not generally recommended. The only means available for making these projections is through an analysis of a detailed, speciated, VOC emissions inventory reflecting the imposition of the VOC control program. Accounting for projected changes in organic reactivity requires that (1) a speciated emissions inventory of acceptable detail is available, and (2) some procedure for estimating how a particular control program may change the reactivity of any source or group of sources. Because of the difficulties associated with each, such projections are likely to contain significant uncertainties, and thus are not generally recommended.

As discussed in the previous section, one additional factor could precipitate the generation of a future case diagram. If the simulation length is shortened in the generation of the base case diagram, then a future diagram using a full, 10-hour simulation period is recommended in order to account for the possibility that the time to peak ozone may increase when VOC controls are implemented. Again, this factor can be incorporated simultaneously with the other potential changes that were discussed above.

Recommended Procedure. Procedures for generating future case diagrams are similar in concept to the recommendations contained in the March 1981 guidelines document. For ozone transport, the recommended procedures are identical. A similar situation exists for NMOC transport, except that only the manmade levels can be reduced, with all background levels held constant. Further, a constant composition of background and manmade transport, from base to future case, is recommended. A similar recommendation exists for the composition of the city's organic composition. However, if an adequate data base exists (i.e., a detailed, speciated emissions inventory), then a shift in organic reactivity can be accommodated, provided sufficient information is available to do so. Finally, if any base-case diagram was generated with a shortened simulation period, then a future case diagram reflecting a simulation length of at least 10 hours is recommended for VOC reduction calculations.

3.5 SELECTION OF THE VOC EMISSION REDUCTION TARGET

After all site/day combinations have been modeled, the final step of the modeling analysis involves the selection of the overall VOC emission reduction target. In essence, this procedure is dictated by the form of the ozone NAAQS, and is identical to the method recommended in the March 1981 guidelines document.[1] In summary, a control target is selected for each site that permits, on average, one hourly-average concentration above 0.12 ppm per year. This corresponds to selecting the fourth highest control level if three years of data are available, the third highest control for two years of data, and the second highest control estimate for only one year. The overall control target is then chosen as the highest of the site specific control estimates to insure that the ozone standard is attained at all sites.

The only additional factor that could affect the procedure just described is the consideration of model predictions versus observations. Recall from Section 3.3.3 that a VOC emission reduction estimate should not be used when the model predicted peak ozone disagrees with the observed peak by more than ±30%. However, it has been observed that substantial underpredictions of base case, peak ozone may lead to control estimates which are too low.[4] Conversely, significant overpredictions of base case, peak ozone may yield control estimates which are too high. Under some circumstances, this finding enables one to use control estimates for those days in which base case, peak ozone is poorly predicted. To illustrate, consider an example in which model predictions and control estimates have been made for a site with three years of ozone data (see Table 3-5). Note that for Day 1, peak ozone is substantially underpredicted, and the control estimate is the highest of all days. If any improvements were made to predicted peak ozone, the control estimate for this day

Table 3-5. Example Illustrating Effect of Model Predictions on Selection of Control Target.

Day	Observed Ozone, ppm	Predicted Ozone, ppm	Relative† Deviation, %	Control Estimate, %	Rank of Control Estimate
1	0.27	0.18	-33	55	1
2	0.22	0.20	- 9	47	3
3	0.20	0.22	+10	51	2
4	0.18	0.18	0	45**	4
5	0.15	0.21	+40	42	5

† Deviation = $\frac{\text{predicted - observed}}{\text{observed}} \times 100$

** Control Target = fourth highest control estimate (for 3 years of data) would likely be increased even more. Since the control estimate for Day 1 is already higher than the control target (i.e., 45%), any improvements in model predictions would not affect the selection of the final control target. Thus, the results from Day 1 can be used, even though the model significantly underpredicted peak ozone. The converse situation occurs for Day 5. In this case, any improvements in model predictions would likely reduce the control estimate for that day, again having no bearing on the choice of the final control target. If the model prediction is poor, but neither of the situations described above occur (i.e., overprediction and high control estimate, or underprediction and low control estimate), then it is recommended that the site/day be discarded, and replaced by the day with the next lowest peak ozone concentration.

Recommended Procedure. To obtain the final VOC emission reduction target, see the procedures described on pages 11 through 16 of the March 1981 guidelines. In general, a candidate control estimate is chosen for each site based on the number of years of data and the statistical form of the ozone standard (i.e., fourth highest control for three years, third highest for two years, and the second highest for one year). Of the candidate site-specific control estimates, the highest one is selected as the overall VOC emission reduction target. However, all cases in which predictions and observations disagree by more than 30%, should be discarded, unless:

(1) peak ozone is underpredicted and the VOC reduction estimate is greater than the candidate site-specific estimate;

(2) peak ozone is overpredicted and the VOC reduction estimate is lower than the candidate site-specific estimate.

In the event that a day is eliminated, the next lowest peak at the site in question should be added for modeling.

4.0 USING THE CB-3 MECHANISM WITH OZIPM

The previous chapter focused on the derivation of model inputs and the modeling procedure for an EKMA/CB-3 application. In this chapter, attention is focused on how the model variables are input to OZIPM. As was mentioned earlier, OZIPM is very similar in structure and operation to the OZIPP model. While a detailed description of these computer programs is beyond the scope of this document, a brief review should facilitate further discussion. For more background information and additional detail, the reader is referred to both the OZIPP and OZIPM User's Manuals, References 2 and 8.

Functionally, the OZIPM program can operate in one of two ways: (1) perform a single simulation in which peak ozone is predicted, and (2) generate an ozone isopleth diagram. The two functions are activated by means of an input record with the code letters CALC or ISOP, respectively, placed in the first four character locations. Additional inputs can follow in one of six 10-column fields: Field 1 includes columns 11-20, Field 2 corresponds to columns 21-30, etc. Other model inputs are handled in a similar manner. Four letter codes are used to identify particular types of model input variables. (Table 4-1 lists several of the more commonly used ones.) Some of these options also require that input data be coded on input records immediately following the option record. In these cases, the data also follow the 10-column field format, except that the fields begin in column 1.

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Table 4-1. Summary of OZIPM Codes For Model Input Data.

CODE	Type of Input Data
MECH	Chemical mechanism
PLAC	Light intensity
DILU	Mixing heights
TRAN	O_3, NMOC and NO_x transport
EMIS	Post-0800 emissions
REAC	Reactivity inputs

All model input variables have been initialized to default values. As a consequence, if any inputs are to be changed, over-riding values must be entered prior to either the CALC option or the ISOP option. As for the numerical data, virtually all inputs are in floating-point format (i.e., decimal rather than integer). In order to minimize the possibility of coding errors, numerical data can always be entered with accompanying decimal points. This convention will be followed throughout this document.

The remaining portion of this chapter deals with the appropriate structure of the model input data that should be used with OZIPM and the CB-3 mechanism. Recall that the CB-3 mechanism is itself an input to OZIPM. As a consequence, the first block of input records in any OZIPM/CB-3 run should always be those input records listed in Appendix B on pages B-2 through B-3. In the discussions below, this block of data will always be indicated by the single code word MECH. Note that this really implies a total of 87 records.

The remainder of this chapter is primarily devoted to the coding and structure of the other model inputs. First, a benchmark run will be discussed so that a prospective user may insure that OZIPM is functioning properly, and that CB-3 is correctly coded. The subsequent sections deal with problems of predicting peak ozone, generating a base case isopleth diagram, and generating a future case diagram.

4.1 OZIPM/CB-3 BENCHMARK

When dealing with a model and chemical mechanism as complex as OZIPM and CB-3, special emphasis should be placed on insuring that the program is operating correctly, and the mechanism has been properly coded and entered to the program. The easiest way to check is by comparison with a benchmark. The input data for the benchmark has been kept as simple as possible in order to avoid the possibility of introducing errors that could be due to some of the other model inputs. Thus, before proceeding to city-specific simulations, replication of the benchmark simulation discussed here is recommended.

The input data required to generate the OZIPM output for comparison with the benchmark are shown in Table 4-2. Note that the MECH option actually indicates all of the CB-3 mechanism inputs (Appendix B) are to be positioned in front of the remaining input records. The DILU option is set so as to eliminate dilution from the simulation. The REAC option is used for organic reactivity input data. The 7.0 (located anywhere within columms 21-30) indicates that there are seven organic compounds whose respective carbon-fractions will follow in the next input record. The order must be the same as that used in the CB-3 mechanism inputs, which in this case is PAR, ETH, OLE, ARO, CARB, DCRB, and NR (see Appendix B). The carbon-fractions used in the benchmark correspond to the default values discussed in Section 3.2.3. They are entered in consecutive 10-column fields (i.e., 1-10, 11-20, 21-30 etc.). Following the reactivity data is the input record instructing OZIPM to perform a single simulation with an initial NMOC concentration of 1.0 (within columns 11-20), and an initial NO_x concentration of 0.100 (within columns 21-30). The value of 1.0 (within columns 31-40) causes a detailed printout of species concentrations, chemical reaction rates, photolytic rate constants, etc. Finally, "blank record" following the CALC option indicates that a blank record is always the last record of an OZIPM input stream.

The output that is generated by OZIPM using the inputs in Table 4-2 is shown in Appendix D. Prospective users should find relatively close agreement between their output and that shown. However, some discrepancies will likely occur as a result of differing computer systems. As a rule of thumb, predicted ozone concentrations should agree fairly closely to the third decimal place. It is also worthwhile to check to insure that all rate constants, especially those for photolytic reactions, are correct. Rate constants for all reactions are printed for each hour of the model simulation (see Appendix D).

4.2 PREDICTION OF PEAK OZONE

Table 4-3 shows the input structure for a sample case in which a single simulation is to be conducted for the purpose of predicting peak ozone. Again, the MECH record is included to indicate the CB-3 input records. Following these records is the record labeled PLAC, which contains information on the city's latitude, longitude, time zone, and the date of the day being modeled (i.e., June 24, 1980 in this example). A free format input record follows, indicating the city's name. The next record contains the initial and maximum afternoon mixing heights. The

Table 4-2. Input Data For Benchmark Run.

```
1    MECH
2    DILU      100.      100.
3    REAC      7.0
4    .58       .04       .03       .19       .05       .00       .15
5    CALC      1.0       .100      1.0
6    BLANK RECORD
```

NOTE: (1) All code words begin in column 1.

(2) The code word MECH represents the 87 records contained in Appendix B.

(3) Numerical entries are contained in 10-column fields (i.e., columns 1-10, 11-20, 21-30, etc.).

(4) "BLANK RECORD" indicates that the last record in an OZIPM input data set should not contain any entries.

Table 4-3. Example Inputs For Predicting Peak Ozone.

```
 1      MECH
 2      PLACE     39.9      75.1      5.0       1980.     6.0       24.0
 3      CITY NAME
 4      DILU      250.      1235.
 5      EMIS      -8.0      .17       .17       .17       .10       .02
 6      .02       .02       .02
 7      .35       .35       .35       .19       .03       .03       .03
 8      .07
 9      REAC      7.0
10      .58       .04       .03       .19       .05       .00       .15
11      TRAN      .01       .07       -7.0      -7.0      0.0       0.0
12      .038      .53       .05       .03       .13       .26       .00
13      .00
14      .040      .61       .06       .03       .15       .15       .00
15      .00
16      CALC      1.10      .120
17      BLANK RECORD
```

NOTE: (1) All code words begin in column 1.

(2) The code word MECH represents the 87 records contained in Appendix B.

(3) Numerical entries are contained in 10-column fields (i.e., columns 1-10, 11-20, 21-30, etc.).

(4) "BLANK RECORD" indicates that the last record in an OZIPM input data set should not contain any entries.

post-0800 emissions data are encoded on the next four records, beginning with the code work EMIS. The reactivity inputs (i.e., REAC) are identical to those discussed in the previous section. The TRAN option is used to input information on transported (and background) pollutants. The first two numerical values are the surface and aloft concentrations of ozone (i.e., 0.01 and 0.07 ppm, respectively). The next two fields are for surface and aloft concentrations of NMOC. The OZIPM convention for entering these data is to code a "-7.0" within columns 31-40 and 41-50. (The minus sign indicates concentration data are to follow, and the seven refers to the number of organic species.) Then the actual input data are coded in the next records, with the first entry giving the total NMOC concentration, and subsequent entries containing the carbon fractions. In this example, 0.038 ppmC is input on the 12th record to account for background reactivity in the surface layer (Table 3-3). The following record indicates that 0.040 ppmC is to be included as manmade transport aloft (see Section 3.2.5). The two sets of carbon-fractions for the seven CB-3 organic species that are shown in Table 3-3 and on page 43 are coded following the total NMOC concentrations within columns 11-20, 21-30, etc. (Note that one additional record is needed to input the carbon fraction for the seventh species in each case, i.e., record numbers 13 and 15.) The final two fields on the TRAN record refer to surface and aloft transport of NO_X, both of which are assumed zero in this example. Finally, the CALC option directs OZIPM to perform a simulation with the initial NMOC and NO_X concentrations shown in the fields following the CALC code. Again, "blank record" following the CALC option refers to the need for a blank input record at the end of the input stream.

The output generated using this input stream is contained in Appendix E. Worthy of note is the fact that the predicted ozone concentrations are printed for each hour of the simulation period. Also note that the maximum 1-hour average concentration occurring during the simulation period is printed near the end of the output. It is this value that is normally compared to the observed peak, as discussed in Section 3.3.

4.3 GENERATING A BASE CASE DIAGRAM

The example discussed in this section is a follow-on to the one just described. Suppose that, using the same model data, the goal is to generate an ozone isopleth diagram rather than make a single prediction of peak ozone. Here, the diagram is presumed to represent existing, or base case, conditions. This can be accomplished by using the same input stream that was used in the previous example, but simply replacing the CALC option with the ISOP option (see Table 4-4). Since no other information is included on the ISOP input record, default values are used to determine the NMOC and NO_x scales on the resultant diagram. Appendix F contains the OZIPM generated output.

4.4 GENERATION OF FUTURE CASE DIAGRAM

The final OZIPM application example is another follow-on to the preceding two examples. The isopleth diagram described in the preceding section represented base case conditions. Assume now that a future case diagram is desired in order to reflect projected changes in ozone aloft and manmade transport. In this example, ozone aloft is reduced from

Table 4-4. Example Inputs For Generating A Base Case Isopleth Diagram.

```
 1    MECH
 2    PLACE     39.9      75.1      5.0       1980.     6.0       24.0
 3    CITY NAME
 4    DILU      250.      1235.
 5    EMIS      -8.0      .17       .17       .17       .10       .02
 6    .02       .02       .02
 7    .35       .35       .35       .19       .03       .03       .03
 8    .07
 9    REAC      7.0
10    .58       .04       .03       .19       .05       .00       .15
11    TRAN      .01       .07       -7.0      -7.0      0.0       0.0
12    .038      .53       .05       .03       .13       .26       .00
13    .00
14    .040      .61       .06       .03       .15       .15       .00
15    .00
16    ISOP
17    BLANK RECORD
```

NOTE: (1) All code words begin in column 1.

(2) The code word MECH represents the 87 records contained in Appendix B.

(3) Numerical entries are contained in 10-column fields (i.e., columns 1-10, 11-20, 21-30, etc.).

(4) "BLANK RECORD" indicates that the last record in an OZIPM input data set should not contain any entries.

0.07 ppm to 0.06 ppm,* and manmade transport of organic compounds from 0.040 ppmC to 0.024 ppmC. As shown in Table 4-5, these are the only inputs that are changed from those needed to generate the base case diagrams. Appendix G contains the output, which differs only slightly from that in Appendix F. The base and future case diagrams shown in these appendices could then be used to compute the VOC emission reduction that is needed to lower the ozone peak observed on this day to a level of 0.12 ppm.

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* Such an estimate is arrived at by using the graph on page 54 of the March 1981 guidelines.

Table 4-5. Example Inputs For Generating A Future Case Isopleth Diagram.

```
 1      MECH
 2      PLACE     39.9      75.1      5.0       1980.     6.0       24.0
 3      CITY NAME
 4      DILU      250.      1235.
 5      EMIS      -8.0      .17       .17       .17       .10       .02
 6      .02       .02       .02
 7      .35       .35       .35       .19       .03       .03       .03
 8      .07
 9      REAC      7.0
10      .58       .04       .03       .19       .05       .00       .15
11      TRAN      .01       .06       -7.0      -7.0      0.0       0.0
12      .038      .53       .05       .03       .13       .26       .00
13      .00
14      .024      .61       .06       .03       .15       .15       .00
15      .00
16      ISOP
17      BLANK RECORD
```

NOTE: (1) All code words begin in column 1.

(2) The code word MECH represents the 87 records contained in Appendix B.

(3) Numerical entries are contained in 10-column fields (i.e., columns 1-10, 11-20, 21-30, etc.).

(4) "BLANK RECORD" indicates that the last record in an OZIPM input data set should not contain any entries.

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APPENDIX A

CB-3 Mechanism Recommended for OZIPM

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Table A-1. CB-3 Mechanism†

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
1.	$NO_2 \longrightarrow NO + O$	1.0*	0
2.	$O + (O_2) + (M) \longrightarrow O_3$	4.40×10^{6}**	0
3.	$NO + O_3 \longrightarrow NO_2 + O_2$	26.6	1450
4.	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	0.048	2450
5.	$NO_2 + O \longrightarrow NO + O_2$	1.3×10^4	0
6.	$OH + O_3 \longrightarrow HO_2 + O_2$	100	1000
7.	$HO_2 + O_3 \longrightarrow OH + 2O_2$	2.40	1525
8.	$OH + NO_2 \longrightarrow HNO_3$	1.60×10^4	0
9.	$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	440	0
10.	$NO + NO + (O_2) \longrightarrow NO_2 + NO_2$	1.50×10^{-4}	0
11.	$NO + NO_3 \longrightarrow NO_2 + NO_2$	2.80×10^4	0
12.	$NO_2 + NO_3 + (H_2O) \longrightarrow 2HNO_3$	26.0	-1.06×10^4
13.	$NO + HO_2 \longrightarrow NO_2 + OH$	1.20×10^4	0
14.	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	1.50×10^4	0
15.	$X + PAR \longrightarrow$	10^5	0
16.	$OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$	1200	560
17.	$O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$	2700	325
18.	$O + OLE \longrightarrow CARB + PAR$	2700	325
19.	$OH + OLE \xrightarrow{O_2} RAO_2$	3.70×10^4	-540
20.	$O_3 + OLE \longrightarrow CARB + CRIG$	0.008	1900
21.	$O_3 + OLE \longrightarrow CARB + MCRG + X$	0.008	1900
22.	$O + ETH \xrightarrow{O_2} MEO_2 + HO_2 + CO$	600	800

Table A-1. CB-3 Mechanism† (continued - 2)

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
23.	$O + ETH \longrightarrow CARB + PAR$	600	800
24.	$OH + ETH \xrightarrow{O_2} RBO_2$	1.20×10^4	-382
25.	$O_3 + ETH \longrightarrow CARB + CRIG$	0.0024	2560
26.	$NO + ACO_3 \xrightarrow{O_2} NO_2 + MEO_2$	1.04×10^4	0
27.	$NO + RBO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2 + CARB$	1.20×10^4	0
28.	$NO + RAO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2 + CARB$	1.20×10^4	0
29.	$NO + MEO_2 \xrightarrow{O_2} NO_2 + CARB + MEO_2 + X$	3700	0
30.	$NO + MEO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2$	7400	0
31.	$NO + MEO_2 \longrightarrow NRAT$	900	0
32.	$O_3 + RBO_2 \longrightarrow CARB + CARB + HO_2 + O_2$	5.0	0
33.	$O_3 + RAO_2 \longrightarrow CARB + CARB + HO_2 + O_2$	20	0
34.	$OH + CARB \longrightarrow CRO_2 + X$	100	0
35.	$OH + CARB \xrightarrow{O_2} HO_2 + CO$	9000	0
36.	$OH + CARB \xrightarrow{O_2} ACO_3 + X$	8200	0
37.	$CARB \longrightarrow CO + H_2$	(0.24)*	0
38a.	$CARB \longrightarrow QQ$	(.564)*	0
38b.	$QQ \xrightarrow{2O_2} HO_2 + HO_2 + CO$	8867	
38c.	$QQ \longrightarrow MEO_2 + MEO_2 + X + XCO$	1133	
38d.	$XCO \longrightarrow X + CO$	10^4	
39.	$NO_2 + ACO_3 \longrightarrow PAN$	7000	0
40.	$PAN \longrightarrow ACO_3 + NO_2$	0.022	1.35×10^4
41.	$HO_2 + ACO_3 \longrightarrow$ stable products	1.50×10^4	0

Table A-1. CB-3 Mechanism† (continued - 3)

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
42.	HO_2 + MEO_2 ---> stable products	9000	0
43.	NO + CRIG ---> NO_2 + CARB	1.20×10^4	0
44.	NO_2 + CRIG ---> NO_3 + CARB	8000	0
45.	CARB + CRIG ---> Ozonide	2000	0
46.	NO + MCRG ---> NO_2 + CARB + PAR	1.20×10^4	0
47.	NO_2 + MCRG ---> NO_3 + CARB + PAR	8000	0
48.	CARB + MCRG ---> Ozonide	2000	0
49.	CRIG ---> CO + H_2O	670**	0
50.	CRIG ---> stable products	240**	0
51.	CRIG $\overset{O_2}{\text{--->}}$ HO_2 + HO_2 + CO	90**	0
52.	MCRG ---> stable products	150**	0
53.	MCRG $\overset{O_2}{\text{--->}}$ MEO_2 + OH + CO	340**	0
54.	MCRG $\overset{O_2}{\text{--->}}$ MEO_2 + HO_2	425**	0
55.	MCRG $\overset{O_2}{\text{--->}}$ CARB + HO_2 + CO + HO_2	85**	0
56.	OH + ARO $\overset{O_2}{\text{--->}}$ RARO + H_2O	6000	600
57.	OH + ARO $\overset{O_2}{\text{--->}}$ HO_2 + OPEN	1.45×10^4	400
58.	NO + RARO $\overset{O_2}{\text{--->}}$ NO_2 + PHEN + HO_2	4000	0
59.	OPEN + NO $\overset{O_2}{\text{--->}}$ NO_2 + DCRB + X + APRC	6000	0
60.	APRC $\overset{O_2}{\text{--->}}$ DCRB + CARB + CO + X	10^4**	0
61.	APRC $\overset{O_2}{\text{--->}}$ CARB + CARB + CO + CO	10^4**	0
62.	PHEN + NO_3 ---> PHO + HNO_3	5000	0
63.	PHO + NO_2 ---> NPHN	4000	0

Table A-1. CB-3 Mechanism† (continued - 4)

	Reaction	Rate Constant at 298 K (ppm^{-1} min^{-1})	Activation Energy (°K)
64.	$PHO + HO_2 \xrightarrow{} PHEN$	5.00×10^4	0
65.	$OPEN + O_3 \xrightarrow{} DCRB + X + APRC$	40	0
66.	$OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + CARB$	3.00×10^4	0
67.	$DCRB \xrightarrow{O_2} HO_2 + ACO_3 + CO$	$(0.02 \times K_1)$***	0
68.	$PHEN + OH \xrightarrow{} PHO$	10^4	0
69.	$CRO_2 + NO \xrightarrow{O_2} NO_2 + CARB + ACO_3 + X$	1.20×10^4	0
70.	$DCRB + OH \xrightarrow{} ACO_3 + CO$	2.5×10^4	0
71.	$HONO \xrightarrow{} OH + NO$	(3.1)*	0
72.	$OH + NO \xrightarrow{} HONO$	9770	0
73.	$O_3 \xrightarrow{} O^1D$	(0.53)*	0
74.	$O^1D \xrightarrow{+(M)} O$	4.44×10^{10}**	0
75.	$O^1D + (H_2O) \xrightarrow{} OH + OH$	6.8×10^9**	0
76.	$O_3 \xrightarrow{} O$	1.0*	

* Sunlight-dependent; rate constant is scaling factor for OZIPM input.

** Units of min^{-1}.

*** Sunlight-dependent; rate constant is scaling factor to be multiplied by rate constant for Reaction 1.

† Source: Reference 9.

APPENDIX B

CB-3 INPUTS FOR OZIPM

This appendix contains a listing, and corresponding explanation, of the inputs that are required to incorporate the CB-3 mechanism in the OZIPM program. The inputs themselves are contained in Table B-1. For reference, each input record has been numbered sequentially. Table B-2 contains a brief explanation of the model input values. For a more comprehensive discussion of these inputs, the reader is referred to Reference 8, the User's Manual for the OZIPM program.

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Table B-1. CB-3 Mechanism Inputs For OZIPM.

```
   1      MECH      99.       7.0       7.0                           1.0
   2      1.        71.       99.       73.       38.       37.       67.
   3      67.
   4      PAR       ETH       OLE       ARO       HCHO      ALD2      NR
   5      1.        2.        2.        6.        1.        3.        1.
   6      NO2              1      NO      O                        1.00E+0
   7      O                2      O3                               4.40E+6
   8      O3    NO         3      NO2                              2.66E+1 1450.0
   9      O3    NO2        4      NO3                               4.8E-2 2450.0
  10      O     NO2        5      NO                               1.30E+4
  11      O3    OH         6      HO2                               1.0E+2 1000.
  12      O3    HO2        7      OH                                2.4E+0 1525.0
  13      NO2   OH         8                                        1.6E+4
  14      CO    OH         9      HO2                               4.4E+2
  15      NO    NO        10      NO2     NO2                      1.50E-4
  16      NO3   NO        11      NO2     NO2                       2.8E+4
  17      NO3   NO2       12                                        2.6E+1 -10600.
  18      HO2   NO        13      NO2     OH                        1.2E+4
  19      HO2   HO2       14                                        1.5E+4
  20      PAR   X         15                                        1.0E+5
  21      PAR   OH        16      MEO2                              1.2E+3 560.0
  22      OLE   O         17      MEO2    ACO3    X                 2.7E+3 325.0
  23      OLE   O         18      HCHO    PAR                       2.7E+3 325.0
  24      OLE   OH        19      RAO2                              3.7E+4 -540.0
  25      OLE   O3        20      HCHO    CRIG                      8.0E-3 1900.0
  26      OLE   O3        21      HCHO    MCRG    X                 8.0E-3 1900.0
  27      ETH   O         22      MEO2    HO2     CO                6.0E+2 800.0
  28      ETH   O         23      HCHO    PAR                       6.0E+2 800.0
  29      ETH   OH        24      RBO2                              1.2E+4 -382.0
  30      ETH   O3        25      HCHO    CRIG                      2.4E-3 2560.0
  31      ACO3  NO        26      NO2     MEO2                     1.04E+4
  32      RBO2  NO        27      NO2     HO2     HCHO    HCHO      1.2E+4
  33      RAO2  NO        28      NO2     HO2     HCHO    HCHO      1.2E+4
  34      MEO2  NO        29      NO2     MEO2    HCHO    X        3.70E+3
  35      MEO2  NO        30      NO2     HCHO    HO2              7.40E+3
  36      MEO2  NO        31                                        9.0E+2
  37      RBO2  O3        32      HCHO    HCHO    HO2               5.0E+0
  38      RAO2  O3        33      HCHO    HCHO    HO2               2.0E+1
  39      OH    HCHO      34      CRO2    X                         1.0E+2
  40      HCHO  OH        35      HO2     CO                        9.0E+3
  41      HCHO  OH        36      X       ACO3                      8.2E+3
  42      HCHO            37      CO                                2.4E-1
  43      HCHO            38      QQ                               5.64E-1
  44      QQ              81      HO2     HO2     CO              8.867E+3
  45      QQ              82      MEO2    MEO2    X       XCO     1.133E+3
  46      XCO             83      X       CO                        1.0E+4
  47      ACO3  NO2       39      PAN                               7.0E+3
  48      PAN             40      ACO3    NO2                       2.2E-2 13500.0
  49      ACO3  HO2       41                                        1.5E+4
  50      MEO2  HO2       42                                        9.0E+3
  51      CRIG  NO        43      NO2     HCHO                      1.2E+4
  52      CRIG  NO2       44      NO3     HCHO                      8.0E+3
  53      CRIG  HCHO      45                                        2.0E+3
  54      MCRG  NO        46      NO2     HCHO    PAR               1.2E+4
  55      MCRG  NO2       47      NO3     HCHO    PAR               8.0E+3
  56      MCRG  HCHO      48                                        2.0E+3
```

Table B-1. CB-3 Mechanism Inputs For OZIPM. (continued)

57	CRIG		49	CO				6.7E+2	
58	CRIG		50					2.4E+2	
59	CRIG		51	HO2	HO2	CO		9.0E+1	
60	MCRG		52					1.5E+2	
61	MCRG		53	MEO2	OH	CO		3.4E+2	
62	MCRG		54	MEO2	HO2			4.25E+2	
63	MCRG		55	HCHO	HO2	HO2	CO	8.5E+1	
64	ARO	OH	56	RARO				6.0E+3	600.0
65	ARO	OH	57	HO2	OPEN			1.45E+4	400.0
66	RARO	NO	58	NO2	PHEN	HO2		4.0E+3	
67	OPEN	NO	59	NO2	ALD2	X	APRC	6.0E+3	
68	APRC		60	ALD2	HCHO	CO	X	1.0E+4	
69	APRC		61	HCHO	HCHO	CO	CO	1.0E+4	
70	PHEN	NO3	62	PHO	HNO3			5.0E+3	
71	PHO	NO2	63					4.0E+3	
72	PHO	HO2	64	PHEN				5.0E+4	
73	OPEN	O3	65	ALD2	X	APRC		4.0E+1	
74	OH	PHEN	66	HO2	APRC	PAR	HCHO	3.0E+4	
75	ALD2		67	HO2	ACO3	CO		2.0E-2	
76	PHEN	OH	68	PHO				1.0E+4	
77	CRO2	NO	69	NO2	HCHO	ACO3	X	1.2E+4	
78	ALD2	OH	70	ACO3	CO			2.5E+4	
79	HONO		71	OH	NO			3.1E0	
80	OH	NO	72	HONO				9.77E+3	
81	O3		73	O1D				5.4E-1	
82	O1D		74	O				4.44E+10	
83	O1D		75	OH	OH			6.8E+9	
84	OH		90	HO2				8.8E+1	
85	OH		91	MEO2				2.8E+1	
86	NR		92	NR				1.0E+0	
87	O3		99	O				1.0E+0	

Table B-2. Explanation of OZIPM/CB-3 Inputs.

Rec #	Columns	Value	Description
1	1- 4	MECH	Signifies mechanism inputs to follow
1	11-13	86.	Identification number of last chemical reaction
1	21-23	7.0	Number of photolytic reactions
1	31-33	7.0	Number of organic species
1	61-63	1.0	Number of photolytic reactions with rates proportional to the NO_2 photolysis rate (k_i)
2	1- 2	1.	Identification number of photolytic reaction 1
2	11-13	71.	Identification number of photolytic reaction 2
2	⋮	⋮	⋮
2	61-63	67.	Identification number of photolytic reaction 7
3	1- 3	67.	Identification number of photolytic reaction with rate proportional to NO_2 photolysis rate (k_i)
4	1- 3	PAR	Name of first organic species
4	11-13	ETH	Name of second organic species
4	⋮	⋮	⋮
4	51-52	NR	Name of seventh organic species
5	1- 2	1.	Carbon number of first organic species
5	11-12	2.	Carbon number of second organic species
5	⋮	⋮	⋮
5	51-52	1.	Carbon number of seventh organic species
6-87*	1- 4	-	Reactant 1
	7-10	-	Reactant 2
	13-16	-	Reactant 3
	17-18	-	Identification number of reaction
	25-28	-	Product 1
	33-36	-	Product 2
	41-44	-	Product 3
	49-52	-	Product 4
	55-64	-	Reaction rate
	66-72	-	Activation energy

* Record numbers 5 through 87 contain the CB-3 chemical reactions. Thus, a general description of the input variables is provided.

APPENDIX C

Computation of Carbon-Bond Fractions From GC Data

In this appendix, the computation of carbon-fractions from results of gas chromotagraphic (GC) analysis is discussed. As noted earlier, GC analysis actually measures the concentrations of individual organic species, which must then be grouped according to the CB-3 organic reactivity classes. In order to keep the computations relatively simple for illustrative purposes, hypothetical examples are discussed. For more detailed discussion, including consideration of "real" data, the reader is referred to References 7 and 9.

At the heart of the computational procedure is the definition of how individual species should be categorized according to carbon bond type. SAI has provided such definitions for approximately 200 individual species, and these are reproduced in Table C-1. These definitions, or species profiles, give the number of bond types found in each CB-3 category. Using this information, along with the carbon numbers shown in Table 3-1, it is possible to compute concentrations of individual carbon bond classes, and then determine percentage of carbon in each class. These computations will be illustrated below by the examples in Tables C-2 and C-3, respectively.

Table C-2 presents example calculations for a hypothetical example. The individual species that might be detected by GC analysis are shown in column 1, and their associated concentrations, in units of ppbC, are shown in column 2. The remaining columns are associated with the carbon bond computations.

Table C-1. Bond Groups Per Molecule (in alphabetical order).

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43814	1,1,1-TRICHLOROETHANE	-	-	-	-	-	2
43820	1,1,2-TRICHLOROETHANE	-	-	-	-	-	2
43813	1,1-DICHLOROETHANE	-	-	-	-	-	2
45225	1,2,3-TRIMETHYLBENZENE	-	3	1	-	-	-
45208	1,2,4-TRIMETHYLBENZENE	-	3	1	-	-	-
45207	1,3,5-TRIMETHYLBENZENE	-	3	1	-	-	-
43218	1,3-BUTADIENE	2	-	-	-	-	-
46201	1,4-DIOXANE	1	2	-	2	-	-
43245	1-HEXENE	1	4	-	-	-	-
43224	1-PENTENE	1	3	-	-	-	-
43312	1-T-2-C-4-TM-CYCLOPENTANE	-	8	-	-	-	-
43296	2,2,3-TRIMETHYLPENTANE	-	8	-	-	-	-
43276	2,2,4-TRIMETHYLPENTANE	-	8	-	-	-	-
43299	2,2,5-TRIMETHYLPENTANE	-	8	-	-	-	-
43291	2,2-DIMETHYLBUTANE	-	6	-	-	-	-
43280	2,3,3-TRIMETHYLPENTANE	-	8	-	-	-	-
43279	2,3,4-TRIMETHYLPENTANE	-	8	-	-	-	-
43234	2,3-DIMETHYL-1-BUTENE	1	4	-	-	-	-
50001	2,3-DIMETHYLBUTANE	-	6	-	-	-	-
43274	2,3-DIMETHYLPENTANE	-	7	-	-	-	-
43277	2,4-DIMETHYLHEXANE	-	8	-	-	-	-
43271	2,4-DIMETHYLPENTANE	-	7	-	-	-	-
43278	2,5-DIMETHYLHEXANE	-	8	-	-	-	-
43308	2-BUTYLETHANOL	-	5	-	1	-	-
43311	2-ETHOXYETHANOL	-	3	-	1	-	-
43452	2-ETHOXYETHYL ACETATE	-	4	-	2	-	-
50002	2-ETHYL-1-BUTENE	1	4	-	-	-	-
43310	2-METHOXYETHANOL	-	2	-	1	-	-
43229	2-METHYL PENTANE	-	6	-	-	-	-
43225	2-METHYL-1-BUTENE	1	3	-	-	-	-
43228	2-METHYL-2-BUTENE	-	3	-	2	-	-
50004	2-METHYL-2-PENTENE	-	4	-	2	-	-
43275	2-METHYLHEXANE	-	7	-	-	-	-
43230	3-METHYL PENTANE	-	6	-	-	-	-
43223	3-METHYL-1-BUTENE	1	3	-	-	-	-
43211	3-METHYL-1-PENTENE	1	4	-	-	-	-
43270	3-METHYL-T-2-PENTENE	-	4	-	2	-	-
43298	3-METHYLHEPTANE	-	8	-	-	-	-
43295	3-METHYLHEXANE	-	7	-	-	-	-
43293	4-METHYL-T-2-PENTENE	-	4	-	2	-	-
43297	4-METHYLHEPTANE	-	8	-	-	-	-
45221	A-METHYLSTYRENE	-	2	1	1	-	-
50025	A-PINENE	1	8	-	-	-	-
43503	ACETALDEHYDE	-	1	-	1	-	-
43404	ACETIC ACID	-	1	-	-	-	1

Table C-1. Bond Groups Per Molecule (in alphabetical order). (continued - 2)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43551	ACETONE	-	3	-	-	-	-
43702	ACETONITRILE	-	1	-	-	-	1
43206	ACETYLENE	-	1	-	-	-	1
43704	ACRYLONITRILE	1	1	-	-	-	-
50015	ANTHRACENE	-	8	1	-	-	-
50020	B-METHYLSTYRENE	1	-	1	1	-	-
50026	B-PINENE	1	8	-	-	-	-
45201	BENZENE	-	1	-	-	-	5
50024	BENZYLCHLORIDE	-	1	1	-	-	-
43213	BUTENE	1	2	-	-	-	-
43510	BUTYRALDEHYDE	-	3	-	1	-	-
50003	C-3-HEXENE	1	4	-	-	-	-
43115	C-7 CYCLOPARAFFINS	-	7	-	-	-	-
43116	C-8 CYCLOPARAFFINS	-	8	-	-	-	-
43117	C-9 CYCLOPARAFFINS	-	9	-	-	-	-
43511	C3 ALDEHYDE	-	2	-	1	-	-
43512	C5 ALDEHYDE	-	4	-	1	-	-
43289	C6 OLEFINS	1	4	-	-	-	-
43294	C7-OLEFINS	1	5	-	-	-	-
43513	C8 ALDEHYDE	-	7	-	1	-	-
43290	C8 OLEFINS	1	6	-	-	-	-
43807	CARBON TETRABROMIDE	-	-	-	-	-	1
43804	CARBON TETRACHLORIDE	-	-	-	-	-	1
43443	CELLOSOLVE ACETATE	-	4	-	2	-	-
43803	CHLOROFORM	-	-	-	-	-	1
43217	CIS-2-BUTENE	-	2	-	2	-	-
43227	CIS-2-PENTENE	-	3	-	2	-	-
50019	CRYOFLOURANE (FREON 114)	-	-	-	-	-	2
43248	CYCLOHEXANE	-	6	-	-	-	-
43264	CYCLOHEXANONE	-	5	-	1	-	-
43273	CYCLOHEXENE	1	4	-	-	-	-
43242	CYCLOPENTANE	-	5	-	-	-	-
43292	CYCLOPENTENE	1	3	-	-	-	-
43207	CYCLOPROPANE	-	3	-	-	-	-
50027	D-LIMONENE	1	6	-	2	-	-
43320	DIACETONE ALCOHOL	-	5	-	1	-	-
43823	DICHLORODIFLUOROMETHANE	-	-	-	-	-	1
43802	DICHLOROMETHANE	-	-	-	-	-	1
50018	DIMETHYL ETHER	-	2	-	-	-	-
43450	DIMETHYL FORMAMIDE	-	-	-	-	-	3
50017	DIMETHYL-2,3,DIHYDRO-1H-INDENE	-	5	1	-	-	-
45103	DIMETHYLETHYLBENZENE	-	4	1	-	-	-
50012	DIMETHYLNAPHTHALENE	-	6	1	-	-	-
43287	DOCOSANE	-	22	-	-	-	-
43285	EICOSANE	-	20	-	-	-	-

Table C-1. Bond Groups Per Molecule (in alphabetical order). (continued - 3)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43202	ETHANE	-	0.4	-	-	-	1.6
43433	ETHYL ACETATE	-	3	-	-	-	1
43438	ETHYL ACRYLATE	-	3	-	2	-	-
43302	ETHYL ALCOHOL	-	2	-	-	-	-
43812	ETHYL CHLORIDE	-	-	-	-	-	2
43351	ETHYL ETHER	-	3	-	1	-	-
43219	ETHYLACETYLENE	-	4	-	-	-	-
43721	ETHYLAMINE	-	1	-	-	-	1
45203	ETHYLBENZENE	-	2	1	-	-	-
43288	ETHYLCYCLOHEXANE	-	8	-	-	-	-
43203	ETHYLENE	-	-	-	-	1	-
43815	ETHYLENE DICHLORIDE	-	-	-	-	1	-
43370	ETHYLENE GLYCOL	-	2	-	-	-	-
43601	ETHYLENE OXIDE	-	1	-	-	-	1
50011	ETHYLNAPHTHALENE	-	6	1	-	-	-
43502	FORMALDEHYDE	-	-	-	1	-	-
43368	GLYCOL	-	1	-	1	-	-
43367	GLYCOL ETHER	-	1	-	1	-	-
43286	HENEICOSANE	-	21	-	-	-	-
43282	HEPTADECANE	-	17	-	-	-	-
43232	HEPTANE	-	7	-	-	-	-
50005	HEPTENE	1	5	-	-	-	-
43281	HEXADECANE	-	16	-	-	-	-
43231	HEXANE	-	6	-	-	-	-
43214	ISO-BUTANE	-	4	-	-	-	-
43306	ISO-BUTYL ALCOHOL	-	4	-	-	-	-
43304	ISO-PROPYL ALCOHOL	-	3	-	-	-	-
43446	ISOBUTYL ACETATE	-	6	-	-	-	-
43451	ISOBUTYL ISOBUTYRATE	-	7	-	1	-	-
43215	ISOBUTYLENE	-	3	-	1	-	-
43120	ISOMERS OF BUTENE	-	2	-	2	-	-
45105	ISOMERS OF BUTYLBENZENE	-	4	1	-	-	-
43109	ISOMERS OF DECANE	-	10	-	-	-	-
45106	ISOMERS OF DIETHYLBENZENE	-	4	1	-	-	-
43112	ISOMERS OF DODECANE	-	12	-	-	-	-
45104	ISOMERS OF ETHYLTOLUENE	-	3	1	-	-	-
43106	ISOMERS OF HEPTANE	-	7	-	-	-	-
43105	ISOMERS OF HEXANE	-	6	-	-	-	-
45234	ISOMERS OF METHYLPROP. BENZENE	-	4	1	-	-	-
43108	ISOMERS OF NONANE	-	9	-	-	-	-
43107	ISOMERS OF OCTANE	-	8	-	-	-	-
43114	ISOMERS OF PENTADECANE	-	15	-	-	-	-
43122	ISOMERS OF PENTANE	-	5	-	-	-	-
43121	ISOMERS OF PENTENE	-	3	-	2	-	-
45108	ISOMERS OF PROPYLBENZENE	-	3	1	-	-	-

Table C-1. Bond Groups Per Molecule (in alphabetical order). (continued - 4)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43113	ISOMERS OF TETRADECANE	-	14	-	-	-	-
43111	ISOMERS OF TRIDECANE	-	13	-	-	-	-
45107	ISOMERS OF TRIMETHYLBENZENE	-	3	1	-	-	-
43110	ISOMERS OF UNDECANE	-	11	-	-	-	-
45102	ISOMERS OF XYLENE	-	2	1	-	-	-
43243	ISOPRENE	1	1	-	2	-	-
43444	ISOPROPYL ACETATE	-	5	-	-	-	-
43119	LACTOL SPIRITS	-	8	-	-	-	-
50022	M-CRESOL (3-METHYLBENZENOL)	-	-	1	1	-	-
45212	M-ETHYLTOLUENE	-	3	1	-	-	-
45205	M-XYLENE	-	2	1	-	-	-
43201	METHANE	-	-	-	-	-	1
43432	METHYL ACETATE	-	-	-	-	-	3
43301	METHYL ALCOHOL	-	1	-	-	-	-
43445	METHYL AMYL ACETATE	-	8	-	-	-	-
43801	METHYL CHLORIDE	-	-	-	-	-	1
43552	METHYL ETHYL KETONE	-	3	-	1	-	-
43560	METHYL ISOBUTYL KETONE	-	5	-	1	-	-
43559	METHYL N-BUTYL KETONE	-	5	-	1	-	-
43209	METHYLACETYLENE	-	1.5	-	-	-	1.5
50016	METHYLANTHRACENE	-	9	1	-	-	-
43261	METHYLCYCLOHEXANE	-	7	-	-	-	-
43262	METHYLCYCLOPENTANE	-	6	-	-	-	-
43272	METHYLCYCLOPENTENE	1	4	-	-	-	-
43819	METHYLENE BROMIDE	-	-	-	-	-	1
50010	METHYLNAPHTHALENE	-	5	1	-	-	-
43118	MINERAL SPIRITS	-	7	-	1	-	-
45801	MONOCHLOROBENZENE	-	5	-	-	-	1
43212	N-BUTANE	-	4	-	-	-	-
43435	N-BUTYL ACETATE	-	5	-	-	-	1
43305	N-BUTYL ALCOHOL	-	4	-	-	-	-
43238	N-DECANE	-	10	-	-	-	-
43255	N-DODECANE	-	12	-	-	-	-
43260	N-PENTADECANE	-	15	-	-	-	-
43220	N-PENTANE	-	5	-	-	-	-
43303	N-PROPYL ALCOHOL	-	3	-	-	-	-
45209	N-PROPYLBENZENE	-	3	1	-	-	-
43259	N-TETRADECANE	-	14	-	-	-	-
43258	N-TRIDECANE	-	13	-	-	-	-
45101	NAPHTHA	-	8	-	-	-	-
43284	NONADECANE	-	19	-	-	-	-
43235	NONANE	-	9	-	-	-	-
50021	O-CRESOL (2-METHYLBENZENOL)	-	-	1	1	-	-
45211	O-ETHYLTOLUENE	-	3	1	-	-	-
45204	O-XYLENE	-	2	1	-	-	-

Table C-1. Bond Groups Per Molecule (in alphabetical order). (continued - 5)

Species Profiles by Bond Group

Saroad No.	Chemical Name	OLE	PAR	ARO	CARB	ETH	UNREACT
43283	OCTADECANE	-	18	-	-	-	-
43233	OCTANE	-	8	-	-	-	-
43265	OCTENE	1	6	-	-	-	-
50023	P-CRESOL (4-METHYLBENZENOL)	-	-	1	1	-	-
45206	P-XYLENE	-	2	1	-	-	-
43817	PERCHLOROETHYLENE	-	-	-	-	-	2
45300	PHENOLS	-	-	-	-	-	6
50006	PROPADIENE	-	1	-	2	-	-
43204	PROPANE	-	1.5	-	-	-	1.5
43504	PROPRIONALDEHYDE	-	2	-	1	-	-
43434	PROPYL ACETATE	-	4	-	-	-	1
43205	PROPYLENE	1	1	-	-	-	-
43369	PROPYLENE GLYCOL	-	2	-	1	-	-
43602	PROPYLENE OXIDE	-	2	-	-	-	1
50013	PROPYLNAPHTHALENE	-	7	1	-	-	-
43208	PROPYNE	-	2	-	-	-	1
45216	SEC-BUTYLBENZENE	-	4	1	-	-	-
45220	STYRENE	-	1	1	1	-	-
43123	TERPENES	1	8	-	-	-	-
43309	TERT-BUTYL ALCOHOL	-	-	-	-	-	4
45215	TERT-BUTYLBENZENE	-	4	1	-	-	-
43390	TETRAHYDROFURAN	-	3	-	1	-	-
45232	TETRAMETHYLBENZENE	-	4	1	-	-	-
45202	TOLUENE	-	1	1	-	-	-
43216	TRANS-2-BUTENE	-	2	-	2	-	-
43226	TRANS-2-PENTENE	-	3	-	2	-	-
45233	TRI/TETRAALKYL BENZENE	-	5	1	-	-	-
43824	TRICHLOROETHYLENE	-	-	-	-	1	-
43811	TRICHLOROFLOUROMETHANE	-	-	-	-	-	1
43821	TRICHLOROTRIFLOUROETHANE	-	-	-	-	-	2
43740	TRIMETHYL AMINE	-	3	-	-	-	-
43822	TRIMETHYLFLUOROSILANE	-	-	-	-	-	3
50014	TRIMETHYLNAPHTHALENE	-	7	1	-	-	-
43241	UNDECANE	-	11	-	-	-	-
43000	UNKNOWN SPECIES	.1	4	.25	.32	.16	-
43860	VINYL CHLORIDE	-	-	-	-	1	-
45401	XYLENE BASE ACIDS	-	2	1	-	-	-

Table C-2. Example Problem† - Part 1

Computation of Carbon Bond Concentrations

Measured Compound		Species Profile*						Carbon-Bond Concentration					
Species	ppbC	PAR	ETH	OLE	ARO	CARB	NR	PAR	ETH	OLE	ARO	CARB	NR
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ethylene	20		1						20				
Propylene	30	1		1				10		20			
n-butane	170	4						170					
Trans-2-butene	10	2				2		5				5	
2,3 dimethyl-butane	100	6						100					
Toluene	70	1			1			10			60		
M-xylene	40	2			1			10			30		
Benzene	60						6						60
Totals	500							305	20	20	90	5	60

* Blank entry corresponds to zero

†This is a hypothetical problem, and is not necessarily intended to be indicative of the NMOC composition of ambient air.

Columns 3-8 show the species profiles, as taken from Table C-1. Columns 9-14 contain concentrations of the individual carbon bond groups that are attributable to the organic compound shown in column 1. These concentrations are calculated according to the following formula:*

$$C_{ij} = \frac{(S_p)_{ij} C_j (C_N)_i}{\sum_{i=1}^{7} (S_p)_{ij} (C_N)_i} \qquad \text{(C-1)}$$

where

C_{ij} = concentration of carbon-bond group i due to species j, ppbC

C_j = measured concentration of species j, ppbC

$(S_p)_{ij}$ = species profile number for carbon-bond group i and species j (Table C-1)

$(C_N)_i$ = carbon number for carbon-bond group i (Table 2-1)

To illustate, consider the apportionment of 30 ppbC of propylene into its individual components. From Table C-1, we see that one bond is defined as olefin and one as paraffin. Thus,

$$C_{PAR} = \frac{(1.0)(30\ \text{ppbc})(1)}{(1.0)(1) + 1.0(2)} = 10\ \text{ppbC}$$

and

$$C_{OLE} = \frac{(1.0)(30\ \text{ppbc})(2)}{(1.0)(1) + 1.0(2)} = 20\ \text{ppbC}$$

---

* In all subsequent formulae, the number 7 refers to the total number of carbon-bond groups requiring inputs: PAR, ETH, OLE, ARO, CARB, DCRB, and NR. However, since DCRB is always zero in this example, it has been omitted from the computations in Tables C-2, C-3 and C-4.

Note that the governing equation, C-1, results in the measured concentration being multiplied by the fraction of carbon defined for each carbon-bond group.

After all of the species concentrations have been apportioned to the carbon-bond groups, then the fraction of carbon corresponding to each group can be calculated. To use the same notation as before:

$$f_i = \frac{\sum_{j=1}^{N} C_{ij}}{\sum_{i=1}^{7} \sum_{j=1}^{N} C_{ij}} \qquad \text{(C-2)}$$

where

f_i = carbon fraction for carbon-bond group i

C_{ij} = concentration of carbon-bond group i due to species j

N = total number of species measured

Stated more simply, the concentrations of each individual carbon bond group are divided by the total concentration measured. Table C-3 shows the results of these computations for the example problem presented in Table C-2. Note that, initially, the sum of carbon-fractions is 1.0. Since oxygenates are not normally measured by GC analysis, 0.04 would be added to carbonyls to account for their presence. Thus, the final set of carbon fractions that is consistent with OZIPM/CB-3 sum to 1.04, and they are shown in the right-hand column of Table C-3.

Table C-3. Example Problem - Part 2

Computation of Carbon Fractions

CB-3 Class	Concentration, ppb[1]	Initial Carbon Fraction[2]	Final Carbon Fraction[3]
PAR	305	0.61	0.61
ETH	20	0.04	0.04
OLE	20	0.04	0.04
ARO	90	0.18	0.18
CARB	5	0.01	0.05
NR	60	0.12	0.12
TOTAL	500	1.00	1.04

---

[1] From Table C-2

[2] Computed by dividing the carbon bond concentration by the total concentration (i.e., 500 ppbc)

[3] CARB adjusted to account for unmeasured oxygenates

The preceding discussion focused on computations associated with the analysis of one GC sample. For OZIPM/CB-3 applications, however, a number of samples are recommended. Since it is extremely unlikely that all samples will yield identical results, some method is required to reconcile differences. The approach recommended here is to average fractions across the samples, and then normalize those results to the value of 1.04. In general notation,

$$\bar{f}_i = \frac{\sum_{k=1}^{K} f_{ik}}{K} \qquad \text{(C-3)}$$

and

$$\hat{f}_i = 1.04 \frac{\bar{f}_i}{\sum_{i=1}^{7} \bar{f}_i} \qquad \text{(C-4)}$$

where

$\bar{f}_i$ = mean carbon-fraction found from K samples

f_{ik} = carbon-fraction for carbon bond group i and sample k

K = total number of samples

$\hat{f}_i$ = normalized carbon-fraction for carbon bond group i

Table C-4 summarizes an example set of computations. Of course, the normalized fractions (right-hand column) would typically be used in an EKMA/CB-3 computation.

Table C-4. Example Problem - Part 3

Computation of Average Carbon Fraction

Species	Carbon Fraction Sample Number 1	2	3	Average[1]	Normalized[2]
PAR	0.61	0.59	0.60	0.60	0.61
ETH	0.04	0.02	0.06	0.04	0.04
OLE	0.04	0.06	0.02	0.03	0.03
ARO	0.18	0.22	0.20	0.20	0.20
CARB	0.05	0.05	0.05	0.05	0.05
NR	0.12	0.10	0.11	0.11	0.11
Total	1.04	1.04	1.04	1.03	1.04

[1] Example: PAR = (0.61 + 0.59 + 0.60)/3 = 0.60

[2] Example: PAR = (1.04/1.03)(0.60) $\approx$ 0.61

APPENDIX D

Output for Benchmark Run

```
THE REACTIONS ARE

  1       NO2           =   NO    O                      1.000+00   0.000
  2       O             =   O3                           4.400+06   0.000
  3       O3     NO     =   NO2                          2.660+01   1.450+03
  4       O3     NO2    =   NO3                          4.800-02   2.450+03
  5       O      NO2    =   NO                           1.300+04   0.000
  6       O3     OH     =   HO2                          1.000+02   1.000+03
  7       O3     HO2    =   OH                           2.400+00   1.525+03
  8       NO2    OH     =                                1.600+04   0.000
  9       CO     OH     =   HO2                          4.400+02   0.000
 10       NO     NO     =   NO2   NO2                    1.500-04   0.000
 11       NO3    NO     =   NO2   NO2                    2.800+04   0.000
 12       NO3    NO2    =                                2.600+01  -1.060+04
 13       HO2    NO     =   NO2   OH                     1.200+04   0.000
 14       HO2    HO2    =                                1.500+04   0.000
 15       PAR    X      =                                1.000+05   0.000
 16       PAR    OH     =   MEO2                         1.200+03   5.600+02
 17       OLE    O      =   MEO2  ACO3  X                2.700+03   3.250+02
 18       OLE    O      =   HCHO  PAR                    2.700+03   3.250+02
 19       OLE    OH     =   RAO2                         3.700+04  -5.400+02
 20       OLE    O3     =   HCHO  CRIG                   8.000-03   1.900+03
 21       OLE    O3     =   HCHO  MCRG  X                8.000-03   1.900+03
 22       ETH    O      =   MEO2  HO2   CO               6.000+02   8.000+02
 23       ETH    O      =   HCHO  PAR                    6.000+02   8.000+02
 24       ETH    OH     =   RBO2                         1.200+04  -3.820+02
 25       ETH    O3     =   HCHO  CRIG                   2.400-03   2.560+03
 26       ACO3   NO     =   NO2   MEO2                   1.040+04   0.000
 27       RBO2   NO     =   NO2   HO2   HCHO  HCHO       1.200+04   0.000
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28        RAO2    NO          =    NO2     HO2     HCHO    HCHO      1.200+04     0.000
29        MEO2    NO          =    NO2     MEO2    HCHO    X         3.700+03     0.000
30        MEO2    NO          =    NO2     HCHO    HO2               7.400+03     0.000
31        MEO2    NO          =                                      9.000+02     0.000
32        RBO2    O3          =    HCHO    HCHO    HO2               5.000+00     0.000
33        RAO2    O3          =    HCHO    HCHO    HO2               2.000+01     0.000
34        OH      HCHO        =    CRO2    X                         1.000+02     0.000
35        HCHO    OH          =    HO2     CO                        9.000+03     0.000
36        HCHO    OH          =    X       ACO3                      8.200+03     0.000
37        HCHO                =    CO                                2.400-01     0.000
38        HCHO                =    QQ                                5.640-01     0.000
81        QQ                  =    HO2     HO2     CO                8.867+03     0.000
82        QQ                  =    MEO2    MEO2    X       XCO       1.133+03     0.000
83        XCO                 =    X       CO                        1.000+04     0.000
39        ACO3    NO2         =    PAN                               7.000+03     0.000
40        PAN                 =    ACO3    NO2                       2.200-02     1.350+04
41        ACO3    HO2         =                                      1.500+04     0.000
42        MEO2    HO2         =                                      9.000+03     0.000
43        CRIG    NO          =    NO2     HCHO                      1.200+04     0.000
44        CRIG    NO2         =    NO3     HCHO                      8.000+03     0.000
45        CRIG    HCHO        =                                      2.000+03     0.000
46        MCRG    NO          =    NO2     HCHO    PAR               1.200+04     0.000
47        MCRG    NO2         =    NO3     HCHO    PAR               8.000+03     0.000
48        MCRG    HCHO        =                                      2.000+03     0.000
49        CRIG                =    CO                                6.700+02     0.000
50        CRIG                =                                      2.400+02     0.000
51        CRIG                =    HO2     HO2     CO                9.000+01     0.000
52        MCRG                =                                      1.500+02     0.000
53        MCRG                =    MEO2    OH      CO                3.400+02     0.000
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54      MCRG            =   MEO2   HO2                   4.250+02   0.000
55      MCRG            =   HCHO   HO2    HO2    CO      8.500+01   0.000
56      ARO    OH       =   RARO                         6.000+03   6.000+02
57      ARO    OH       =   HO2    OPEN                  1.450+04   4.000+02
58      RARO   NO       =   NO2    PHEN   HO2            4.000+03   0.000
59      OPEN   NO       =   NO2    ALD2   X      APRC    6.000+03   0.000
60      APRC            =   ALD2   HCHO   CO     X       1.000+04   0.000
61      APRC            =   HCHO   HCHO   CO     CO      1.000+04   0.000
62      PHEN   NO3      =   PHO    HNO3                  5.000+03   0.000
63      PHO    NC2      =                                4.000+03   0.000
64      PHO    HO2      =   PHEN                         5.000+04   0.000
65      OPEN   O3       =   ALD2   X      APRC           4.000+01   0.000
66      OH     PHEN     =   HO2    APRC   PAR    HCHO    3.000+04   0.000
67      ALD2            =   HO2    ACO3   CO             2.000-02   0.000
68      PHEN   OH       =   PHO                          1.000+04   0.000
69      CRO2   NO       =   NO2    HCHO   ACO3   X       1.200+04   0.000
70      ALD2   OH       =   ACO3   CO                    2.500+04   0.000
71      HONO            =   OH     NO                    3.100+00   0.000
72      OH     NO       =   HONO                         9.770+03   0.000
73      O3              =   O1D                          5.400-01   0.000
74      O1D             =   O                            4.440+10   0.000
75      O1D             =   OH     OH                    6.800+09   0.000
90      OH              =   HO2                          8.800+01   0.000
91      OH              =   MEO2                         2.800+01   0.000
92      NR              =   NR                           1.000+00   0.000
99      O3              =   O                            1.000+00   0.000
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PHOTOLYTIC RATE CONSTANTS CALCULATED FOR

        LOS ANGELES, CALIF.

LATITUDE     34.058

LONGITUDE    118.250

TIME ZONE    8.0

DATE         6     21   1975

TIME         800   TO   1800     LOCAL DAYLIGHT TIME

SOLAR NOON   1300


DILUTION DETERMINED FROM THE FOLLOWING

INVERSION HEIGHTS     INITIAL   100.     FINAL       100.

TIMING                START     800.     STOP       1617.


MIXING HEIGHTS (AT THE BEGINNING OF EACH HOUR)

TIME       800    900    1000   1100   1200   1300   1400   1500   1600

HEIGHT    100.0  100.0  100.0  100.0  100.0  100.0  100.0  100.0  100.0



INITIAL         PAR  FRACTION  .580   ETH  FRACTION  .040   OLE  FRACTION  .030

INITIAL         ARO  FRACTION  .190   HCHO FRACTION  .050   ALD2 FRACTION  .000

INITIAL         NR   FRACTION  .150

NO2/NOX        .250

THERE ARE NO ALDEHYDES IN THE MECHANISM
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THE ERROR TOLERANCE IS   1.000-02

THE RATE CONSTANTS USED WERE

     2.763-01    4.400+06    2.882+01    5.497-02    1.300+04    1.057+02    2.611+00    1.600+04    4.400+02    1.500-04

     2.800+04    1.446+01    1.200+04    1.500+04    1.000+05    1.238+03    2.749+03    2.749+03    3.591+04    8.888-03

     8.388-03    6.272+02    6.272+02    1.175+04    2.766-03    1.040+04    1.200+04    1.200+04    3.700+03    7.400+03

     9.000+02    5.000+00    2.000+01    1.000+02    9.000+03    8.200+03    5.672-04    4.202-04    7.000+03    4.646-02

     1.500+04    9.000+03    1.200+04    8.000+03    2.000+03    1.200+04    8.000+03    2.000+03    6.700+02    2.400+02

     9.000+01    1.500+02    3.400+02    4.250+02    8.500+01    6.203+03    1.482+04    4.000+03    6.000+03    1.000+04

     1.000+04    5.000+03    4.000+03    5.000+04    4.000+01    3.000+04    5.525-03    1.000+04    1.200+04    2.500+04

     5.140-02    9.770+03    3.164-04    4.440+10    6.800+09    0.000       0.000       0.000       0.000       0.000

     8.867+03    1.133+03    1.000+04    0.000       0.000       0.000       0.000       0.000       0.000       8.800+01

     2.800+01    1.000+00    0.000       0.000       0.000       0.000       0.000       0.000       2.074-02

THE PHOTOLYSIS REACTIONS ARE

           1          71          99          73          38          37          67

THE PHOTOLYTIC RATE CONSTANTS ARE

        2.763-01    5.140-02    2.074-02    3.164-04    4.202-04    5.672-04    5.525-03
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                        TIME      HC      PROPYLENE    ALDEHYDE     NOX        NO2        O3
                        (LDT )    TOTAL   FRACTION     FRACTION     TOTAL      FRACTION   (INSTANT)

                        800.      1.04000   .00000       .00000      .10000      .25000     .00000

 TIME        NO2        NO         O          O3         NO3        OH         HO2        CO         PAR        X
 INTERVAL    MEO2       OLE        ACO3       HCHO       RAO2       CRIG       MCRG       ETH        RBO2       CRO2
             QQ         PAN        ARO        RARO       OPEN       PHEN       ALD2       APRC       FHO        HNO3
             HONO       O10        XCO        NR

 8.000+02    2.500-02   7.500-02   0.000      0.000      0.000      0.000      0.000      0.000      5.800-01   0.000
 1.000-10    0.000      1.500-02   0.000      5.000-02   0.000      0.000      0.000      2.000-02   0.000      0.000
             0.000      0.000      3.167-02   0.000      0.000      0.000      0.000      0.000      0.000      0.000
             0.000      0.000      0.000      1.500-01

NET RATES   -6.905-03   6.905-03   6.906-03   0.000      0.000      0.000      0.000      2.836-05   0.000      0.000
             0.000      0.000      0.000     -4.937-05   0.000      0.000      0.000      0.000      0.000      0.000
             2.101-05   0.000      0.000      0.000      0.000      0.000      0.000      0.000      0.000      0.000
             0.000      0.000      0.000      0.000

THE REACTION RATES ARE
      6.91-03     0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       8.44-07
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       2.84-05    2.10-05    0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
      0.00        1.50-01    0.00       0.00       0.00       0.00       0.00       0.00       0.00       0.00
                                                                                               0.00
THE PHOTOLYTIC RATE CONSTANTS ARE

      2.763-01    5.140-02   2.074-02   3.164-04   4.202-04   5.672-04   5.525-03
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                     TIME      HC      PROPYLENE   ALDEHYDE     NOX        NO2        O3
                     (LDT )   TOTAL     FRACTION    FRACTION    TOTAL     FRACTION   (INSTANT)

                     900.   1.02040     .00769      .00000     .09526     .48316     .01196

 TIME       NO2        NO          O          O3         NO3         OH         HO2         CO         PAR         X
INTERVAL    MEO2       OLE         ACO3       HCHO       RAO2        CRIG       MCRG        ETH        RBO2        CRO2
            QQ         PAN         ARO        RARO       OPEN        FHEN       ALD2        AFRC       PHO         HNO3
            HONO       O1D         XCO        HR

 9.000+02   4.603-02   4.923-02   4.016-09   1.196-02   2.220-08   1.215-07   8.096-07   1.058-02   5.678-01   3.979-09
 6.704+00   4.097-07   1.252-02   1.340-07   6.031-02   9.230-08   9.402-10   6.400-10   1.887-02   4.553-08   1.238-09
            4.188-09   4.995-04   2.860-02   1.093-07   1.739-07   8.193-04   2.617-03   2.724-09   5.898-09   1.146-06
            8.313-04   1.845-16   4.745-10   1.500-01

NET RATES   4.619-04  -5.896-04   1.689-06   3.435-04   1.288-07  -5.890-07   3.236-07   2.696-04  -3.075-04  -1.283-07
            1.166-07  -5.753-05   6.159-08   2.566-04   3.931-08  -4.938-10  -4.980-10  -2.765-05   2.724-08   1.126-09
            2.606-09   1.996-05  -7.305-05   2.091-08   4.796-08   1.746-05   5.102-05  -4.690-08  -1.883-11   9.096-08
           -1.204-06   1.200-08   4.775-12   0.000

THE REACTION RATES ARE
     1.74-02    1.77-02    1.70-02    3.03-05    2.40-06    1.54-07    2.53-08    8.94-05    5.65-07    3.64-07
     3.06-05    1.48-08    4.78-04    9.83-09    2.26-04    8.54-05    1.38-07    1.38-07    5.46-05    1.33-06
     1.33-06    4.75-08    4.75-08    2.69-05    6.24-07    6.86-05    2.69-05    5.45-05    7.46-05    1.49-04
     1.82-05    2.72-09    2.21-08    7.33-07    6.59-05    6.01-05    5.19-05    4.19-05    4.32-05    2.32-05
     1.63-09    2.98-09    5.55-07    3.46-07    1.13-07    3.78-07    2.36-07    7.72-08    6.30-07    2.26-07
     8.46-08    9.60-08    2.18-07    2.72-07    5.44-08    2.15-05    5.15-05    2.15-05    5.14-05    2.72-05
     2.72-05    9.10-08    1.09-06    2.39-10    8.32-08    2.99-06    1.97-05    9.95-07    7.31-07    7.95-06
     5.96-05    5.84-05    9.46-06    8.19-06    1.25-06    0.00       0.00       0.00       0.00       0.00
     3.71-05    4.75-06    4.75-06    0.00       0.00       0.00       0.00       0.00       0.00       1.07-05
     3.40-06    1.50-01    0.00       0.00       0.00       0.00       0.00       0.00       3.10-04

THE PHOTOLYTIC RATE CONSTANTS ARE

     3.771-01   7.173-02   2.591-02   7.909-04   6.944-04   8.601-04   7.542-03
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                               TIME        HC      PROPYLENE    ALDEHYDE      NOX          NO2         O3
                              (LDT )      TOTAL    FRACTION     FRACTION     TOTAL      FRACTION    (INSTANT)

                              1000.      .98237     .01497       .00000      .08401      .76410      .04722

   TIME         NO2         NO          O           O3          NO3         OH          HO2         CO          PAR         X
 INTERVAL       MEO2        OLE         ACO3        HCHO        RAO2        CRIG        MCRG        ETH         RBO2        CRO2
                QQ          PAN         ARO         RARO        OPEN        PHEN        ALD2        APRC        PHO         HNO3
                HONO        O1D         XCO         NR

  1.000+03    6.419-02    1.982-02    6.772-09    4.722-02    2.924-07    1.553-07    2.708-06    3.119-02    5.464-01    5.544-09
  9.692+00    1.325-06    8.989-03    4.506-07    7.526-02    2.083-07    3.162-09    1.992-09    1.702-02    1.289-07    4.832-09
              6.898-09    2.947-03    2.399-02    2.883-07    4.526-07    1.696-03    4.902-03    3.158-09    1.982-08    4.905-05
              4.253-04    1.224-15    7.816-10    1.500-01

 NET RATES   -2.901-04    3.524-05   -5.488-06    1.209-03    4.292-06   -9.073-06    5.438-06    4.136-04   -3.984-04   -1.845-06
              1.758-06   -5.802-05    1.132-06    2.170-04    3.915-07   -1.780-08   -1.682-08   -3.343-05    3.776-07    1.968-08
             -2.622-09    6.552-05   -7.835-05    2.572-07    5.650-07    9.841-06    2.388-05   -5.814-07    2.164-08    2.479-06
             -6.225-06    3.107-07    5.116-12    0.000

 THE REACTION RATES ARE
        2.84-02     2.98-02     2.70-02     1.67-04     5.65-06     7.75-07     3.34-07     1.60-04     2.13-06     5.89-08
        1.62-04     2.71-07     6.44-04     1.10-07     3.03-04     1.05-04     1.67-07     1.67-07     5.01-05     3.77-06
        3.77-06     7.23-08     7.23-08     3.11-05     2.22-06     9.29-05     3.07-05     4.95-05     9.71-05     1.94-04
        2.36-05     3.04-08     1.97-07     1.17-06     1.05-04     9.59-05     8.11-05     6.90-05     2.02-04     1.37-04
        1.83-08     3.23-08     7.52-07     1.62-06     4.76-07     4.74-07     1.02-06     3.00-07     2.12-06     7.59-07
        2.85-07     2.99-07     6.77-07     8.47-07     1.69-07     2.31-05     5.52-05     2.29-05     5.33-05     3.16-05
        3.16-05     2.48-06     5.09-06     2.68-09     8.55-07     7.90-06     4.33-05     2.63-06     1.15-06     1.90-05
        3.63-05     3.01-05     6.30-05     5.43-05     8.32-06     0.00        0.00        0.00        0.00        0.00
        6.12-05     7.82-06     7.82-06     0.00        0.00        0.00        0.00        0.00        0.00        1.37-05
        4.35-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        1.37-03
 THE PHOTOLYTIC RATE CONSTANTS ARE

      4.420-01    8.536-02    2.904-02    1.334-03    9.166-04    1.078-03    8.840-03
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                    TIME      HC      PROPYLENE   ALDEHYDE     NOX         NO2        O3
                   (LDT )    TOTAL    FRACTION    FRACTION    TOTAL      FRACTION  (INSTANT)

                   1100.     .92853    .01891      .00000     .06485      .87887     .11359

   TIME        NO2        NO          O          O3         NO3        OH         HO2        CO         PAR        X
 INTERVAL      MEO2       OLE         ACO3       HCHO       RAO2       CRIG       MCRG       ETH        RBO2       CRO2
               QQ         PAN         ARO        RARO       OPEN       PHEN       ALD2       APRC       PHO        HNO3
               HONO       O1D         XCO        NR

  1.100+03    5.700-02   7.856-03   7.083-09   1.136-01   1.564-06   2.127-07   8.846-06   6.041-02   5.191-01   7.722-09
  5.000+00    4.229-06   5.587-03   1.345-06   8.663-02   4.421-07   5.968-09   3.273-09   1.478-02   3.894-07   1.954-08
              9.287-09   8.741-03   1.909-02   8.012-07   1.165-06   1.869-03   5.851-03   3.606-09   8.141-08   5.098-04
              1.977-04   4.001-15   1.052-09   1.500-01

 NET RATES   -2.681-04  -1.198-04  -1.938-07   1.304-03   1.217-07  -1.825-07   2.876-07   5.606-04  -5.236-04  -3.469-08
              1.211-07  -5.418-05   7.751-08   1.522-04   8.973-09  -4.400-10  -4.264-10  -4.172-05   1.481-08   9.618-10
             -3.098-10   1.304-04  -8.541-05   1.833-08   2.535-08  -5.317-06   8.787-06  -9.305-09   2.425-09   1.462-05
             -2.226-06   4.577-09   3.638-12   0.000

 THE REACTION RATES ARE
       2.74-02    3.12-02    2.57-02    3.56-04    5.25-06    2.55-06    2.62-06    1.94-04    5.65-06    9.26-09
       3.44-04    1.29-06    8.34-04    1.17-06    4.01-04    1.37-04    1.09-07    1.09-07    4.27-05    5.64-06
       5.64-06    6.57-08    6.57-08    3.69-05    4.64-06    1.10-04    3.67-05    4.17-05    1.23-04    2.46-04
       2.99-05    2.21-07    1.00-06    1.84-06    1.66-04    1.51-04    1.06-04    9.29-05    5.37-04    4.06-04
       1.78-07    3.37-07    5.63-07    2.72-06    1.03-06    3.09-07    1.49-06    5.67-07    4.00-06    1.43-06
       5.37-07    4.91-07    1.11-06    1.39-06    2.78-07    2.52-05    6.02-05    2.52-05    5.49-05    3.61-05
       3.61-05    1.46-05    1.86-05    3.60-08    5.29-06    1.19-05    5.63-05    3.98-06    1.84-06    3.11-05
       1.86-05    1.63-05    2.05-04    1.78-04    2.72-05    0.00       0.00       0.00       0.00       0.00
       8.23-05    1.05-05    1.05-05    0.00       0.00       0.00       0.00       0.00       0.00       1.87-05
       5.96-06    1.50-01    0.00       0.00       0.00       0.00       0.00       0.00       3.55-03

 THE PHOTOLYTIC RATE CONSTANTS ARE

          4.815-01     9.385-02     3.125-02     1.804-03     1.072-03     1.223-03     9.629-03
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                        TIME      HC      PROPYLENE     ALDEHYDE      NOX         NO2        O3
                       (LDT )    TOTAL    FRACTION      FRACTION     TOTAL      FRACTION   (INSTANT)

                        1200.    .85555    .02083        .00000      .03830       .92809     .19956

  TIME        NO2         NO          O           O3          NO3         OH          HO2         CO          PAR         X
 INTERVAL     MEO2        OLE         ACO3        HCHO        RAO2        CRIG        MCRG        ETH         RBO2        CRO2
              QQ          PAN         ARO         RARO        OPEN        PHEN        ALD2        APRC        PHO         HNO3
              HONO        OID         XCO         NR

  1.200+03    3.554-02    2.754-03    5.615-09    1.996-01    4.712-06    2.990-07    2.926-05    9.809-02    4.829-01    1.051-08
  1.000+01    1.463-05    2.725-03    4.357-06    9.231-02    7.902-07    7.636-09    3.217-09    1.203-02    1.240-06    8.332-08
              1.073-08    1.891-02    1.383-02    2.324-06    2.505-06    1.158-03    5.940-03    3.583-09    2.140-07    1.832-03
              9.600-05    8.236-15    1.216-09    1.500-01

NET RATES    -4.186-04   -5.405-05    5.477-08    1.506-03   -2.747-08   -2.307-07    2.261-07    6.819-04   -6.747-04   -1.896-07
              5.247-07   -3.900-05    1.207-06    2.378-05   -1.304-08    4.682-10    3.858-10   -4.897-05    3.551-08    6.748-09
             -4.834-10    2.053-04   -8.698-05    5.407-08   -5.113-08   -1.523-05   -6.873-06    9.063-08    1.204-08    2.729-05
             -1.404-06   -8.255-09    1.478-12    0.000

THE REACTION RATES ARE
        1.79-02     2.47-02     1.58-02     3.90-04     2.59-06     6.31-06     1.52-05     1.70-04     1.29-05     1.14-09
        3.63-04     2.42-06     9.67-04     1.28-05     5.07-04     1.79-04     4.21-08     4.21-08     2.93-05     4.83-06
        4.83-06     4.24-08     4.24-08     4.22-05     6.64-06     1.25-04     4.10-05     2.61-05     1.49-04     2.98-04
        3.63-05     1.24-06     3.15-06     2.76-06     2.48-04     2.26-04     1.20-04     1.07-04     1.08-03     8.79-04
        1.91-06     3.85-06     2.52-07     2.17-06     1.41-06     1.06-07     9.15-07     5.94-07     5.12-06     1.83-06
        6.87-07     4.83-07     1.09-06     1.37-06     2.73-07     2.57-05     6.13-05     2.56-05     4.14-05     3.58-05
        3.58-05     2.73-05     3.04-05     3.13-07     2.00-05     1.04-05     5.97-05     3.46-06     2.75-06     4.44-05
        9.45-06     8.04-06     4.22-04     3.66-04     5.60-05     0.00        0.00        0.00        0.00        0.00
        9.51-05     1.22-05     1.22-05     0.00        0.00        0.00        0.00        0.00        0.00        2.63-05
        8.37-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        6.49-03

THE PHOTOLYTIC RATE CONSTANTS ARE

      5.024-01     9.841-02     3.251-02     2.113-03     1.162-03     1.303-03     1.005-02
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                       TIME      HC       PROPYLENE    ALDEHYDE     NOX        NO2        O3
                      (LDT )    TOTAL     FRACTION     FRACTION    TOTAL     FRACTION  (INSTANT)

                       1300.    .77528     .01908       .00000     .01418     .95150     .27750

    TIME        NO2         NO          O           O3          NO3         OH          HO2         CO          PAR         X
  INTERVAL      MEO2        OLE         ACO3        HCHO        RAO2        CRIG        MCRG        ETH         RBO2        CRO2
                QQ          PAN         ARO         RARO        OPEN        PHEN        ALD2        APRC        PHO         HNO3
                HONO        O1D         XCO         NR

  1.300+03    1.349-02    6.879-04    3.750-09    2.775-01    9.521-06    2.684-07    7.099-05    1.374-01    4.439-01    9.150-09
  1.000+01    4.657-05    1.087-03    1.635-05    8.912-02    7.602-07    7.609-09    2.077-09    9.329-03    3.028-06    2.849-07
              1.059-08    3.062-02    9.433-03    5.619-06    2.467-06    4.248-04    4.930-03    2.048-09    3.719-07    3.351-03
              2.573-05    1.198-14    1.200-09    1.500-01

 NET RATES   -2.793-04    2.641-05   -1.991-06    9.617-04    1.450-06   -3.374-06   -4.551-07    5.744-04   -5.500-04   -2.067-06
              1.916-06   -1.586-05    2.583-05   -1.235-04   -2.147-08   -1.050-08   -8.051-09   -3.662-05    2.218-07    4.034-08
             -2.643-08    1.215-04   -5.323-05    2.408-07   -3.399-08   -7.998-06   -2.513-05    1.674-08   -3.529-08    2.022-05
             -7.611-07   -3.084-07   -1.592-12    0.000


 THE REACTION RATES ARE
      6.86-03     1.65-02     5.50-03     2.06-04     6.58-07     7.87-06     5.14-05     5.79-05     1.62-05     7.10-11
      1.83-04     1.86-06     5.86-04     7.56-05     4.06-04     1.47-04     1.12-08     1.12-08     1.05-05     2.68-06
      2.68-06     2.19-08     2.19-08     2.94-05     7.16-06     1.17-04     2.50-05     6.28-06     1.19-04     2.37-04
      2.88-05     4.20-06     4.22-06     2.39-06     2.15-04     1.96-04     1.18-04     1.06-04     1.54-03     1.42-03
      1.74-05     2.98-05     6.28-08     8.21-07     1.36-06     1.71-08     2.24-07     3.70-07     5.10-06     1.83-06
      6.65-07     3.12-07     7.06-07     8.83-07     1.77-07     1.57-05     3.75-05     1.55-05     1.02-05     2.05-05
      2.05-05     2.02-05     2.01-05     1.32-06     2.74-05     3.42-06     5.01-05     1.14-06     2.35-06     3.31-05
      2.56-06     1.80-06     6.13-04     5.32-04     8.14-05     0.00        0.00        0.00        0.00        0.00
      9.39-05     1.20-05     1.20-05     0.00        0.00        0.00        0.00        0.00        0.00        2.36-05
      7.51-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        9.11-03

 THE PHOTOLYTIC RATE CONSTANTS ARE

        5.082-01    9.966-02    3.283-02    2.209-03    1.188-03    1.326-03    1.016-02
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                               TIME      HC        PROPYLENE     ALDEHYDE      NOX          NO2        O3
                               (LDT )    TOTAL     FRACTION      FRACTION      TOTAL        FRACTION   (INSTANT)

                               1400.     .71992      .01436       .00000       .00529       .95954      .31212

 TIME          NO2          NO           O            O3           NO3          OH           HO2          CO           PAR          X
 INTERVAL      MEO2         OLE          ACO3         HCHO         RAO2         CRIG         MCRG         ETH          RBO2         CRO2
               QQ           PAN          ARO          RARO         OPEN         PHEN         ALD2         APRC         PHO          HNO3
               HONO         O1D          XCO          NR

  1.400+03     5.080-03     2.142-04     3.000-09     3.121-01
  4.248+00     8.693-05     5.035-04     4.543-05     8.077-02     1.275-05     1.660-07     7.520-05     1.656-01     4.190-01     5.516-09
               9.295-09     3.463-02     7.244-03     8.659-06     3.410-07     6.648-09     1.159-09     7.660-03     3.616-06     5.201-07
               4.597-06     1.263-14     1.053-09     1.500-01     1.295-06     1.576-04     3.447-03     9.309-10     4.280-07     4.218-03

 NET RATES    -5.475-05    -2.584-06    -1.049-07
               5.103-07    -5.803-06     1.034-06     3.389-04     4.985-08    -1.185-08    -1.986-07     3.882-04    -3.163-04    -1.891-08
              -1.302-09     6.521-06    -2.528-05    -1.481-04    -4.569-09    -1.609-10    -9.068-11    -2.158-05    -4.901-10     3.408-09
              -1.025-07    -2.353-08    -2.956-12     3.849-08    -1.049-08    -2.063-06    -2.162-05     4.691-10    -1.196-09     1.004-05
                                                      0.000

 THE REACTION RATES ARE
      2.54-03      1.32-02      1.93-03      8.72-05      1.98-07      5.47-06      6.13-05      1.35-05      1.21-05      6.88-12
      7.65-05      9.36-07      1.93-04      8.48-05      2.31-04      8.61-05      4.15-09      4.15-09      3.00-06      1.40-06
      1.40-06      1.44-08      1.44-08      1.49-05      6.61-06      1.01-04      9.29-06      8.77-07      6.89-05      1.39-04
      1.68-05      5.64-06      2.13-06      1.34-06      1.21-04      1.10-04      1.04-04      9.29-05      1.62-03      1.61-03
      5.13-05      5.83-05      1.71-08      2.70-07      1.07-06      2.98-09      4.71-08      1.87-07      4.45-06      1.60-06
      5.98-07      1.74-07      3.94-07      4.93-07      9.86-08      7.46-06      1.78-05      7.42-06      1.66-06      9.31-06
      9.31-06      1.00-05      8.70-06      1.61-06      1.62-05      7.85-07      3.45-05      2.62-07      1.34-06      1.43-05
      4.50-07      3.47-07      6.46-04      5.61-04      8.59-05      0.00         0.00         0.00         0.00         0.00
      8.24-05      1.05-05      1.05-05      0.00         0.00         0.00         0.00         0.00         0.00         1.46-05
      4.65-06      1.50-01      0.00         0.00         0.00         0.00         0.00         0.00         1.01-02
 THE PHOTOLYTIC RATE CONSTANTS ARE

      4.998-01     9.785-02     3.236-02     2.071-03     1.151-03     1.293-03     9.997-03
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                     TIME        HC       PROPYLENE     ALDEHYDE      NOX         NO2          O3
                    (LDT )     TOTAL      FRACTION      FRACTION     TOTAL      FRACTION    (INSTANT)

                    1500.     .68184       .01063        .00000      .00387      .96339       .32756

  TIME        NO2          NO           O            O3           NO3          OH           HO2          CO           PAR          X
INTERVAL      MEO2         OLE          ACO3         HCHO         RAO2         CRIG         MCRG         ETH          RBO2         CRO2
              QQ           PAN          ARO          RARO         OPEN         PHEN         ALD2         APRC         FHO          HNO3
              HONO         O1D          XCO          HR

  1.500+03    3.729-03     1.417-04     2.819-09     3.276-01     1.511-05     1.371-07     6.511-05     1.860-01     4.027-01     4.275-09
  1.933+01    1.002-04     2.578-04     5.879-05     7.234-02     1.536-07     5.673-09     6.384-10     6.536-03     3.155-06     5.846-07
              7.596-09     3.361-02     6.001-03     9.054-06     8.736-07     8.640-05     2.417-03     6.274-10     3.665-07     4.699-03
              2.169-06     1.110-14     8.606-10     1.500-01

NET RATES    -4.837-06    -2.849-06    -7.956-06     2.180-04     4.791-08    -1.252-07    -2.100-08     2.956-04    -2.401-04     8.784-08
             -2.082-08    -2.773-06    -3.550-06    -1.263-04     1.037-09    -1.830-09    -5.160-10    -1.647-05    -8.460-09    -2.665-09
             -5.147-08    -2.693-05    -1.729-05    -3.008-08     4.274-09    -6.764-07    -1.283-05    -4.972-09    -1.379-08     6.527-06
             -1.123-08    -1.210-06    -2.842-12     0.000

THE REACTION RATES ARE
       1.77-03     1.24-02     1.34-03     6.72-05     1.37-07     4.74-06     5.57-05     8.18-06     1.12-05     3.01-12
       5.99-05     8.15-07     1.11-04     6.36-05     1.72-04     6.83-05     2.00-09     2.00-09     1.27-06     7.50-07
       7.50-07     1.16-08     1.16-08     1.05-05     5.92-06     8.66-05     5.37-06     2.61-07     5.25-05     1.05-04
       1.28-05     5.17-06     1.01-06     9.91-07     8.92-05     8.13-05     8.69-05     7.59-05     1.53-03     1.56-03
       5.74-05     5.87-05     9.65-09     1.69-07     8.21-07     1.09-09     1.90-08     9.24-08     3.80-06     1.36-06
       5.11-07     9.58-08     2.17-07     2.71-07     5.43-08     5.10-06     1.22-05     5.13-06     7.43-07     6.27-06
       6.27-06     6.53-06     5.47-06     1.19-06     1.14-05     3.55-07     2.30-05     1.18-07     9.94-07     8.28-06
       2.01-07     1.90-07     5.67-04     4.93-04     7.55-05     0.00        0.00        0.00        0.00        0.00
       6.74-05     8.61-06     8.61-06     0.00        0.00        0.00        0.00        0.00        0.00        1.21-05
       3.84-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        1.01-02

THE PHOTOLYTIC RATE CONSTANTS ARE

      4.760-01     9.266-02     3.092-02     1.731-03     1.049-03     1.202-03     9.520-03
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                            TIME       HC       PROPYLENE    ALDEHYDE      NOX         NO2         O3
                           (LDT )     TOTAL     FRACTION     FRACTION     TOTAL      FRACTION   (INSTANT)

                           1600.     .64685      .00787       .00000      .00405      .96825      .34207

 TIME         NO2         NO          O           O3          NO3         OH          HO2         CO          PAR         X
INTERVAL      MEO2        OLE         ACO3        HCHO        RAO2        CRIG        MCRG        ETH         RBO2        CRO2
              QQ          PAN         ARO         RARO        OPEN        PHEN        ALD2        APRC        PHO         HNO3
              HONO        O1D         XCO         NR

 1.600+03   3.919-03    1.285-04    2.600-09    3.421-01    1.904-05    1.078-07    5.306-05    2.051-01    3.867-01    3.217-09
 2.344+00   8.795-05    1.166-04    5.142-05    6.446-02    5.390-08    4.738-09    3.050-10    5.444-03    2.124-06    4.519-07
            5.300-09    3.108-02    4.917-03    6.468-06    5.438-07    4.415-05    1.698-03    4.001-10    2.320-07    5.108-03
            1.749-06    7.247-15    6.004-10    1.500-01

NET RATES  -5.891-05    6.510-05    3.524-04   -1.694-04    6.656-08    5.526-09    3.932-07    2.081-04   -1.758-04   -1.677-11
           -2.369-07   -1.162-06    4.277-07   -8.588-05   -7.976-10   -1.013-11   -2.859-12   -1.206-05   -1.399-03   -2.184-09
            3.834-06   -3.317-05   -1.114-05   -3.775-08   -3.943-09   -4.533-07   -7.394-06   -2.650-12   -1.799-09    4.203-06
           -1.028-08    5.272-05   -3.467-12    0.000

THE REACTION RATES ARE
      1.69-03     1.14-02     1.27-03     7.37-05     1.32-07     3.90-06     4.74-05     6.76-06     9.72-06     2.48-12
      6.85-05     1.08-06     8.18-05     4.22-05     1.24-04     5.16-05     8.33-10     8.33-10     4.51-07     3.54-07
      3.54-07     8.88-09     8.88-09     6.89-06     5.15-06     6.87-05     3.27-06     8.31-08     4.18-05     8.36-05
      1.02-05     3.63-06     3.69-07     6.95-07     6.25-05     5.70-05     6.73-05     5.68-05     1.41-03     1.44-03
      4.09-05     4.20-05     7.31-09     1.49-07     6.11-07     4.70-10     9.56-09     3.93-08     3.17-06     1.14-06
      4.26-07     4.58-08     1.04-07     1.30-07     2.59-08     3.29-06     7.86-06     3.32-06     4.19-07     4.00-06
      4.00-06     4.20-06     3.64-06     6.16-07     7.44-06     1.43-07     1.47-05     4.76-08     6.97-07     4.57-06
      1.46-07     1.35-07     4.24-04     3.22-04     4.93-05     0.00        0.00        0.00        0.00        0.00
      4.70-05     6.00-06     6.00-06     0.00        0.00        0.00        0.00        0.00        0.00        9.48-06
      3.02-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        9.78-03
THE PHOTOLYTIC RATE CONSTANTS ARE

        4.323-01    8.325-02    2.858-02    1.239-03    8.816-04    1.044-03    8.647-03
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                          TIME      HC      PROPYLENE    ALDEHYDE      NOX          NO2         O3
                         (LDT )    TOTAL    FRACTION    .FRACTION     TOTAL      FRACTION   (INSTANT)

                         1700.    .63312     .00684       .00000      .00437      .97214      .34889

  TIME        NO2         NO          O          O3          NO3         OH          HO2         CO          PAR          X
INTERVAL      MEO2        OLE         ACO3       HCHO        RAO2        CRIG        MCRG        ETH         RBO2         CRO2
              QQ          PAN         ARO        RARO        OPEN        PHEN        ALD2        APRC        PHO          HNO3
              HONO        O1D         XCO        NR

 1.700+03    4.248-03    1.217-04    2.393-09    3.489-01    2.262-05    8.390-08    4.505-05    2.128-01    3.800-01    2.521-09
 2.000+01    7.679-05    7.672-05    4.533-05    6.166-02    2.740-08    4.349-09    2.053-10    4.976-03    1.535-06    3.558-07
             4.005-09    2.969-02    4.507-03    4.890-06    3.820-07    2.659-05    1.443-03    2.838-10    1.577-07    5.263-03
             1.532-06    4.751-15    4.538-10    1.500-01

NET RATES    8.672-06   -9.266-08    8.941-08    1.461-04    1.282-07    8.965-09   -2.029-07    1.546-04   -1.352-04    5.874-09
            -2.811-07   -7.079-07   -2.939-07   -5.186-05   -1.054-10   -9.479-11   -3.906-11   -9.721-06   -1.418-08   -2.378-09
            -9.823-11   -3.128-05   -7.952-06   -3.590-08   -3.307-09   -3.596-07   -5.058-06    5.970-11   -5.443-09    3.007-06
            -5.879-09   -5.099-08   -3.411-12    0.000


THE REACTION RATES ARE
      1.54-03     1.05-02     1.22-03     8.15-05     1.32-07     3.09-06     4.11-05     5.70-06     7.85-06     2.22-12
      7.71-05     1.39-06     6.58-05     3.04-05     9.58-05     3.95-05     5.05-10     5.05-10     2.31-07     2.38-07
      2.38-07     7.47-09     7.47-09     4.91-06     4.80-06     5.74-05     2.24-06     4.00-08     3.46-05     6.92-05
      8.41-06     2.68-06     1.91-07     5.17-07     4.66-05     4.24-05     5.04-05     4.01-05     1.35-03     1.38-03
      3.06-05     3.11-05     6.35-09     1.48-07     5.36-07     3.00-10     6.98-09     2.53-08     2.91-06     1.04-06
      3.91-07     3.08-08     6.98-08     8.73-08     1.75-08     2.35-06     5.61-06     2.38-06     2.79-07     2.84-06
      2.84-06     3.01-06     2.68-06     3.55-07     5.33-06     6.69-08     1.05-05     2.23-08     5.20-07     3.03-06
      1.06-07     9.98-08     2.43-04     2.11-04     3.23-05     0.00        0.00        0.00        0.00        0.00
      3.55-05     4.54-06     4.54-06     0.00        0.00        0.00        0.00        0.00        0.00        7.38-06
      2.35-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        8.78-03

THE PHOTOLYTIC RATE CONSTANTS ARE

      3.630-01    6.899-02    2.516-02    6.971-04    6.495-04    8.170-04    7.259-03
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                            TIME     HC       PROPYLENE    ALDEHYDE     NOX        NO2        O3
                            (LDT )   TOTAL    FRACTION     FRACTION     TOTAL      FRACTION   (INSTANT)

                            1800.    .62082    .00577       .00000      .00494     .98055     .35609

TIME          NO2        NO         O          O3         NO3        OH         HO2        CO         PAR        X
INTERVAL      MEO2       OLE        ACO3       HCHO       RAO2       CRIG       MCRG       ETH        RBO2       CRO2
              QQ         PAN        ARO        RARO       OPEN       PHEN       ALD2       AFRC       PHO        HNO3
              HONO       O1D        XCO        NR

  1.800+03    4.839-03   9.598-05   1.875-09   3.561-01   3.375-05   4.454-08   3.120-05   2.200-01   3.737-01   1.414-09
  1.000+01    6.004-05   4.560-05   3.758-05   5.955-02   8.832-09   3.934-09   1.245-10   4.483-03   8.037-07   2.318-07
              2.191-09   2.795-02   4.154-03   3.054-06   1.853-07   8.849-06   1.195-03   1.379-10   7.172-08   5.397-03
              1.090-06   1.746-15   2.482-10   1.500-01

NET RATES     9.969-06  -9.064-07  -9.433-07   8.939-05   3.474-07   7.442-10  -2.734-07   8.591-05  -7.341-05   1.719-09
             -2.675-07  -3.620-07  -8.437-08  -2.005-05  -1.439-10  -2.156-11  -3.732-12  -6.771-06  -1.090-08  -1.786-09
             -2.033-10  -2.564-05  -3.890-06  -2.482-08  -2.652-09  -2.247-07  -3.231-06  -8.258-12  -3.026-09   1.493-06
             -8.762-09   3.059-08  -3.411-12   0.000

THE REACTION RATES ARE
        1.22-03     8.25-03     9.85-04     9.47-05     1.18-07     1.68-06     2.90-05     3.45-06     4.31-06     1.38-12
        9.07-05     2.36-06     3.59-05     1.46-05     5.28-05     2.06-05     2.35-10     2.35-10     7.29-08     1.44-07
        1.44-07     5.27-09     5.27-09     2.35-06     4.42-06     3.75-05     9.26-07     1.02-08     2.13-05     4.26-05
        5.19-06     1.43-06     6.29-08     2.65-07     2.39-05     2.17-05     2.99-05     2.19-05     1.27-03     1.30-03
        1.76-05     1.69-05     4.53-09     1.52-07     4.69-07     1.43-10     4.82-09     1.48-08     2.64-06     9.44-07
        3.54-07     1.87-08     4.23-08     5.29-08     1.06-08     1.15-06     2.74-06     1.17-06     1.07-07     1.38-06
        1.38-06     1.49-06     1.39-06     1.12-07     2.64-06     1.18-08     6.02-06     3.94-09     2.67-07     1.33-06
        5.05-08     4.18-08     8.94-05     7.75-05     1.19-05     0.00        0.00        0.00        0.00        0.00
        1.94-05     2.48-06     2.48-06     0.00        0.00        0.00        0.00        0.00        0.00        3.92-06
        1.25-06     1.50-01     0.00        0.00        0.00        0.00        0.00        0.00        6.95-03
THE PHOTOLYTIC RATE CONSTANTS ARE

        2.521-01     4.637-02     1.952-02     2.511-04     3.678-04     5.022-04     5.041-03

                        MAXIMUM O3    NOT REACHED, THE LAST ONE HOUR AVERAGE WAS .35277 PPM.
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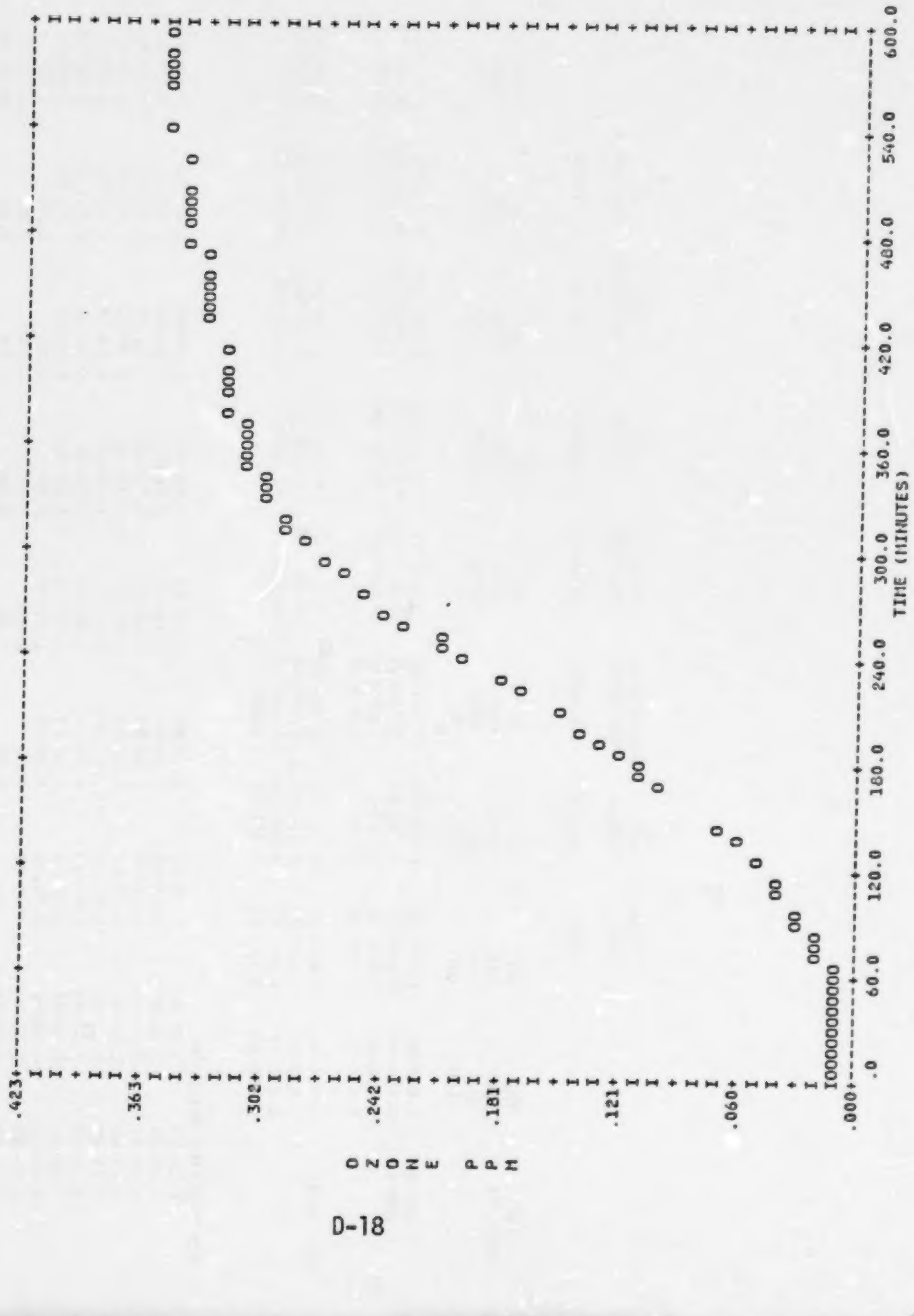

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600.0
TIME (MINUTES)

APPENDIX E

OZIPM Output Corresponding to Inputs Shown in Table 4-3

```
THE REACTIONS ARE

     1        NO2             =    NO     O                           1.000+00   0.000
     2        0               =    O3                                 4.400+06   0.000
     3        O3     NO       =    NO2                                2.660+01   1.450+03
     4        O3     NO2      =    NO3                                4.800-02   2.450+03
     5        O      NO2      =    NO                                 1.300+04   0.000
     6        O3     OH       =    HO2                                1.000+02   1.000+03
     7        O3     HO2      =    OH                                 2.400+00   1.525+03
     8        NO2    OH       =                                       1.600+04   0.000
     9        CO     OH       =    HO2                                4.400+02   0.000
    10        NO     NO       =    NO2    NO2                         1.500-04   0.000
    11        NO3    NO       =    NO2    NO2                         2.800+04   0.000
    12        NO3    NO2      =                                       2.600+01  -1.060+04
    13        HO2    NO       =    NO2    OH                          1.200+04   0.000
    14        HO2    HO2      =                                       1.500+04   0.000
    15        PAR    X        =                                       1.000+05   0.000
    16        PAR    OH       =    MEO2                               1.200+03   5.600+02
    17        OLE    O        =    MEO2   ACO3   X                    2.700+03   3.250+02
    18        OLE    O        =    HCHO   PAR                         2.700+03   3.250+02
    19        OLE    OH       =    RAO2                               3.700+04  -5.400+02
    20        OLE    O3       =    HCHO   CRIG                        8.000-03   1.900+03
    21        OLE    O3       =    HCHO   MCRG   X                    8.000-03   1.900+03
    22        ETH    O        =    MEO2   HO2    CO                   6.000+02   8.000+02
    23        ETH    O        =    HCHO   PAR                         6.000+02   8.000+02
    24        ETH    OH       =    RBO2                               1.200+04  -3.820+02
    25        ETH    O3       =    HCHO   CRIG                        2.400-03   2.560+03
    26        ACO3   NO       =    NO2    MEO2                        1.040+04   0.000
    27        RBO2   NO       =    NO2    HO2    HCHO   HCHO          1.200+04   0.000
```

```
28        RAO2   NO        =    NO2    HO2    HCHO   HCHO    1.200+04   0.000
29        MEO2   NO        =    NO2    MEO2   HCHO   X       3.700+03   0.000
30        MEO2   NO        =    NO2    HCHO   HO2            7.400+03   0.000
31        MEO2   NO        =                                 9.000+02   0.000
32        RBO2   O3        =    HCHO   HCHO   HO2            5.000+00   0.000
33        RAO2   O3        =    HCHO   HCHO   HO2            2.000+01   0.000
34        OH     HCHO      =    CRO2   X                     1.000+02   0.000
35        HCHO   OH        =    HO2    CO                    9.000+03   0.000
36        HCHO   OH        =    X      ACO3                  8.200+03   0.000
37        HCHO             =    CO                           2.400-01   0.000
38        HCHO             =    QQ                           5.640-01   0.000
81        QQ               =    HO2    HO2    CO             8.867+03   0.000
82        QQ               =    MEO2   MEO2   X      XCO     1.133+03   0.000
83        XCO              =    X      CO                    1.000+04   0.000
39        ACO3   NO2       =    PAN                          7.000+03   0.000
40        PAN              =    ACO3   NO2                   2.200-02   1.350+04
41        ACO3   HO2       =                                 1.500+04   0.000
42        MEO2   HO2       =                                 9.000+03   0.000
43        CRIG   NO        =    NO2    HCHO                  1.200+04   0.000
44        CRIG   NO2       =    NO3    HCHO                  8.000+03   0.000
45        CRIG   HCHO      =                                 2.000+03   0.000
46        MCRG   NO        =    NO2    HCHO   PAR            1.200+04   0.000
47        MCRG   NO2       =    NO3    HCHO   PAR            8.000+03   0.0[illegible]
48        MCRG   HCHO      =                                 2.000+03   0.00[illegible]
49        CRIG             =    CO                           6.700+02   0.000
50        CRIG             =                                 2.400+02   0.000
51        CRIG             =    HO2    HO2    CO             9.000+01   0.000
52        MCRG             =                                 1.500+02   0.000
53        MCRG             =    MEO2   OH     CO             3.400+02   0.000
```

```
54      MCRG            =   MEO2   HO2                     4.250+02   0.000
55      MCRG            =   HCHO   HO2    HO2     CO       8.500+01   0.000
56      ARO     OH      =   RARO                           6.000+03   6.000+02
57      ARO     OH      =   HO2    OPEN                    1.450+04   4.000+02
58      RARO    NO      =   NO2    PHEN   HO2              4.000+03   0.000
59      OPEN    NO      =   NO2    ALD2   X       APRC     6.000+03   0.000
60      AFRC            =   ALD2   HCHO   CO      X        1.000+04   0.000
61      APRC            =   HCHO   HCHO   CO      CO       1.000+04   0.000
62      PHEN    NO3     =   PHO    HNO3                    5.000+03   0.000
63      PHO     NO2     =                                  4.000+03   0.000
64      PHO     HO2     =   PHEN                           5.000+04   0.000
65      OPEN    O3      =   ALD2   X      APRC             4.000+01   0.000
66      OH      PHEN    =   HO2    APRC   PAR     HCHO     3.000+04   0.000
67      ALD2            =   HO2    ACO3   CO               2.000-02   0.000
68      PHEN    OH      =   PHO                            1.000+04   0.000
69      CRO2    NO      =   NO2    HCHO   ACO3    X        1.200+04   0.000
70      ALD2    OH      =   ACO3   CO                      2.500+04   0.000
71      HONO            =   OH     NO                      3.100+00   0.000
72      OH      NO      =   HONO                           9.770+03   0.000
73      O3              =   O1D                            5.400-01   0.000
74      O1D             =   O                              4.440+10   0.000
75      O1D             =   OH     OH                      6.800+09   0.000
90      OH              =   HO2                            8.800+01   0.000
91      OH              =   MEO2                           2.800+01   0.000
92      NR              =   NR                             1.000+00   0.000
99      O3              =   O                              1.000+00   0.000
```

```
PHOTOLYTIC RATE CONSTANTS CALCULATED FOR

        CITY NAME

LATITUDE     39.900

LONGITUDE     75.100

TIME ZONE    5.0

DATE         6     24   1980

TIME         800   TO   1800     LOCAL DAYLIGHT TIME

SOLAR NOON   1303


DILUTION DETERMINED FROM THE FOLLOWING

INVERSION HEIGHTS     INITIAL   250.     FINAL      1235.

TIMING                START     800.     STOP       1617.


MIXING HEIGHTS (AT THE BEGINNING OF EACH HOUR)

TIME        800    900   1000   1100   1200   1300   1400   1500   1600   1700

HEIGHT     250.0  411.5  614.3  804.4  945.1 1044.5 1117.5 1174.3 1222.1 1235.0



INITIAL         PAR  FRACTION  .580   ETH  FRACTION  .040   OLE  FRACTION  .030

INITIAL         ARO  FRACTION  .190   HCHO FRACTION  .050   ALD2 FRACTION  .000

INITIAL         NR   FRACTION  .150

NO2/NOX        .250

THERE ARE NO ALDEHYDES IN THE MECHANISM


TRANSPORTED CONCENTRATIONS
```

```
SURFACE LAYER        OZONE    .010     HYDROCARBON   .038    NOX       .000 PPM

ALOFT                OZONE    .070     HYDROCARBON   .040    NOX       .000 PPM


CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTON OF INITIAL

NON-BACKGROUND HYDROCARBON CONCENTRATION EMITTED PER HOUR)

    HOUR        1     2     3     4     5     6     7     8

    FRACTION  .170  .170  .170  .100  .020  .020  .020  .020


CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTION OF INITIAL

NON-BACKGROUND NOX CONCENTRATION EMITTED PER HOUR)

    HOUR        1     2     3     4     5     6     7     8

    FRACTION  .350  .350  .350  .190  .030  .030  .030  .070
```

```
 TIME     HC      PROPYLENE    ALDEHYDE     NOX          NO2       O3
(LDT )   TOTAL    FRACTION     FRACTION     TOTAL       FRACTION  (INSTANT)

 800.   1.18200     .00000      .00000     .12000       .25000     .01000

 900.    .83869     .00552      .00000     .09471       .58620     .01801

1000.    .63663     .01028      .00000     .07448       .73878     .04154

1100.    .53564     .01385      .00000     .06161       .80845     .06715

1200.    .46497     .01721      .00000     .04718       .85920     .09945

1300.    .39670     .01988      .00000     .02987       .89736     .13992

1400.    .34065     .01976      .00000     .01505       .92485     .18129

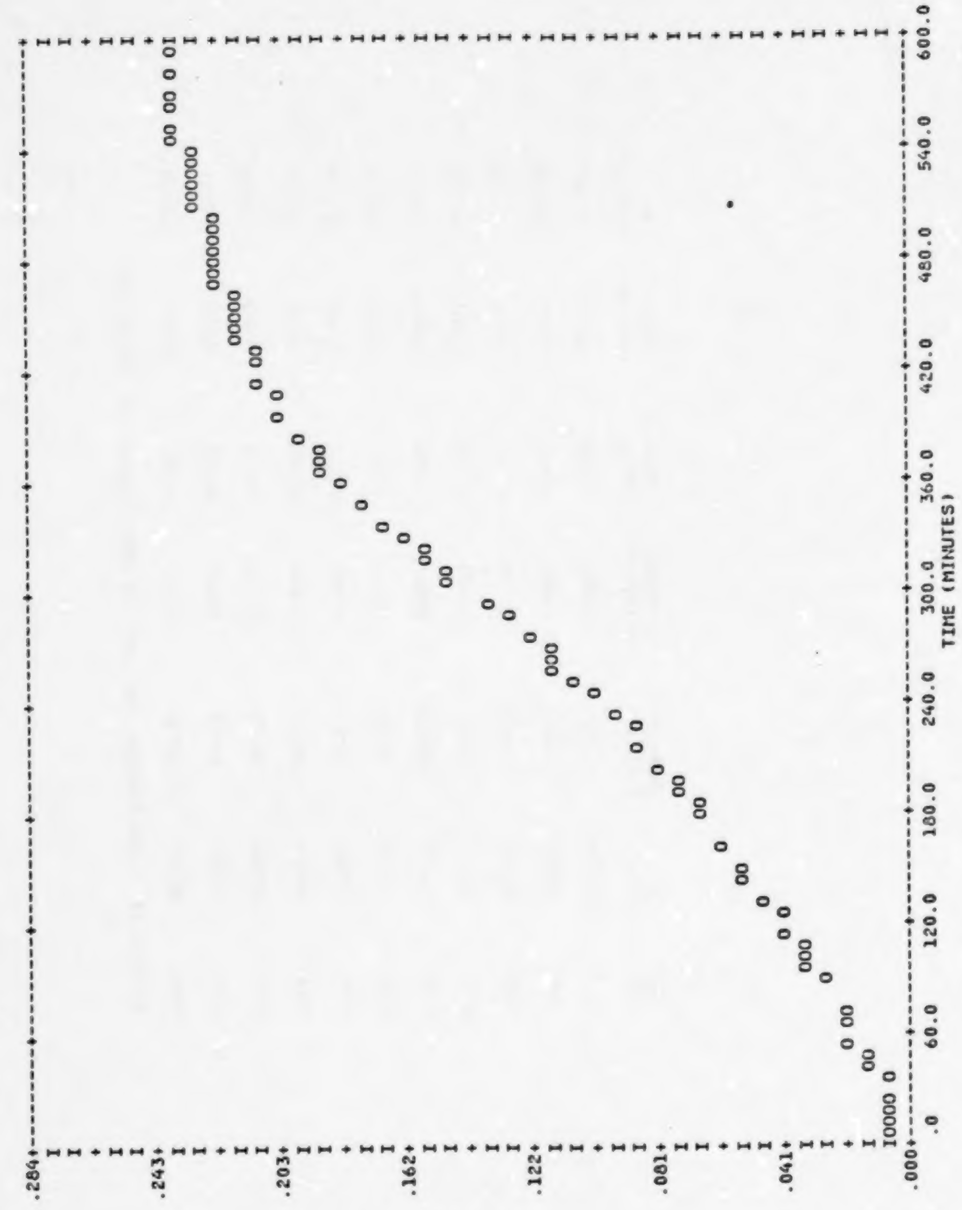
1500.    .29911     .01628      .00000     .00675       .93988     .20889

1600.    .26518     .01170      .00000     .00435       .95027     .22408

1700.    .25575     .00983      .00000     .00383       .95662     .23211

1800.    .24733     .00791      .00000     .00386       .96736     .23989

 MAXIMUM O3    NOT REACHED, THE LAST ONE HOUR AVERAGE WAS .23630 PPM.
```


OZONE PPM
.284
.243
.203
.162
.122
.081
.041
.000
.0
60.0
120.0
180.0
240.0
300.0
360.0
420.0
480.0
540.0
600.0
TIME (MINUTES)

APPENDIX F

OZIPM Output Corresponding To Inputs Shown in Table 4-4

```
THE REACTIONS ARE

   1          NO2                =    NO     O                        1.000+00    0.000
   2          O                  =    O3                              4.400+06    0.000
   3          O3      NO         =    NO2                             2.660+01    1.450+03
   4          O3      NO2        =    NO3                             4.800-02    2.450+03
   5          O       NO2        =    NO                              1.300+04    0.000
   6          O3      OH         =    HO2                             1.000+02    1.000+03
   7          O3      HO2        =    OH                              2.400+00    1.525+03
   8          NO2     OH         =                                    1.600+04    0.000
   9          CO      OH         =    HO2                             4.400+02    0.000
  10          NO      NO         =    NO2    NO2                      1.500-04    0.000
  11          NO3     NO         =    NO2    NO2                      2.800+04    0.000
  12          NO3     NO2        =                                    2.600+01   -1.060+04
  13          HO2     NO         =    NO2    OH                       1.200+04    0.000
  14          HO2     HO2        =                                    1.500+04    0.000
  15          PAR     X          =                                    1.000+05    0.000
  16          PAR     OH         =    MEO2                            1.200+03    5.600+02
  17          OLE     O          =    MEO2   ACO3   X                 2.700+03    3.250+02
  18          OLE     O          =    HCHO   PAR                      2.700+03    3.250+02
  19          OLE     OH         =    RAO2                            3.700+04   -5.400+02
  20          OLE     O3         =    HCHO   CRIG                     8.000-03    1.900+03
  21          OLE     O3         =    HCHO   MCRG   X                 8.000-03    1.900+03
  22          ETH     O          =    MEO2   HO2    CO                6.000+02    8.000+02
  23          ETH     O          =    HCHO   PAR                      6.000+02    8.000+02
  24          ETH     OH         =    RBO2                            1.200+04   -3.820+02
  25          ETH     O3         =    HCHO   CRIG                     2.400-03    2.560+03
  26          ACO3    NO         =    NO2    MEO2                     1.040+04    0.000
  27          RBO2    NO         =    NO2    HO2    HCHO   HCHO       1.200+04    0.000
```

```
28     RAO2   NO      =   NO2    HO2    HCHO   HCHO     1.200+04   0.000
29     MEO2   NO      =   NO2    MEO2   HCHO   X        3.700+03   0.000
30     MEO2   NO      =   NO2    HCHO   HO2             7.400+03   0.000
31     MEO2   NO      =                                 9.000+02   0.000
32     RBO2   O3      =   HCHO   HCHO   HO2             5.000+00   0.000
33     RAO2   O3      =   HCHO   HCHO   HO2             2.000+01   0.000
34     OH     HCHO    =   CRO2   X                      1.000+02   0.000
35     HCHO   OH      =   HO2    CO                     9.000+03   0.000
36     HCHO   OH      =   X      ACO3                   8.200+03   0.000
37     HCHO           =   CO                            2.400-01   0.000
38     HCHO           =   QQ                            5.640-01   0.000
81     QQ             =   HO2    HO2    CO              8.867+03   0.000
82     QQ             =   MEO2   MEO2   X      XCO      1.133+03   0.000
83     XCO            =   X      CO                     1.000+04   0.000
39     ACO3   NO2     =   PAN                           7.000+03   0.000
40     PAN            =   ACO3   NO2                    2.200-02   1.350+04
41     ACO3   HO2     =                                 1.500+04   0.000
42     MEO2   HO2     =                                 9.000+03   0.000
43     CRIG   NO      =   NO2    HCHO                   1.200+04   0.000
44     CRIG   NO2     =   NO3    HCHO                   8.000+03   0.000
45     CRIG   HCHO    =                                 2.000+03   0.000
46     MCRG   NO      =   NO2    HCHO   PAR             1.200+04   0.000
47     MCRG   NO2     =   NO3    HCHO   PAR             8.000+03   0.000
48     MCRG   HCHO    =                                 2.000+03   0.000
49     CRIG           =   CO                            6.700+02   0.000
50     CRIG           =                                 2.400+02   0.000
51     CRIG           =   HO2    HO2    CO              9.000+01   0.000
52     MCRG           =                                 1.500+02   0.000
53     MCRG           =   MEO2   OH     CO              3.400+02   0.000
```

```
54     MCRG            =   MEO2   HO2                    4.250+02   0.000
55     MCRG            =   HCHO   HO2    HO2    CO       8.500+01   0.000
56     ARO    OH       =   RARO                          6.000+03   6.000+02
57     ARO    OH       =   HO2    OPEN                   1.450+04   4.000+02
58     RARO   NO       =   NO2    PHEN   HO2             4.000+03   0.000
59     OPEN   NO       =   NO2    ALD2   X      APRC     6.000+03   0.000
60     APRC            =   ALD2   HCHO   CO     X        1.000+04   0.000
61     APRC            =   HCHO   HCHO   CO     CO       1.000+04   0.000
62     PHEN   NO3      =   PHO    HNO3                   5.000+03   0.000
63     PHO    NO2      =                                 4.000+03   0.000
64     PHO    HO2      =   PHEN                          5.000+04   0.000
65     OPEN   O3       =   ALD2   X      APRC            4.000+01   0.000
66     OH     PHEN     =   HO2    APRC   PAR    HCHO     3.000+04   0.000
67     ALD2            =   HO2    ACO3   CO              2.000-02   0.000
68     PHEN   OH       =   PHO                           1.000+04   0.000
69     CRO2   NO       =   NO2    HCHO   ACO3   X        1.200+04   0.000
70     ALD2   OH       =   ACO3   CO                     2.500+04   0.000
71     HONO            =   OH     NO                     3.100+00   0.000
72     OH     NO       =   HONO                          9.770+03   0.000
73     O3              =   O1D                           5.400-01   0.000
74     O1D             =   O                             4.440+10   0.000
75     O1D             =   OH     OH                     6.800+09   0.000
90     OH              =   HO2                           8.800+01   0.000
91     OH              =   MEO2                          2.800+01   0.000
92     NR              =   NR                            1.000+00   0.000
99     O3              =   O                             1.000+00   0.000
```

```
PHOTOLYTIC RATE CONSTANTS CALCULATED FOR

      CITY NAME

LATITUDE     39.900

LONGITUDE     75.100

TIME ZONE    5.0

DATE         6     24    1980

TIME         800   TO    1800     LOCAL DAYLIGHT TIME


DILUTION DETERMINED FROM THE FOLLOWING

INVERSION HEIGHTS     INITIAL   250.     FINAL      1235.

TIMING                START     800.     STOP       1617.


MIXING HEIGHTS (AT THE BEGINNING OF EACH HOUR)

TIME       800    900   1000   1100   1200   1300   1400   1500   1600   1700

HEIGHT   250.0  411.5  614.3  804.4  945.1 1044.5 1117.5 1174.3 1222.1 1235.0


INITIAL        PAR  FRACTION  .580   ETH  FRACTION  .040   OLE  FRACTION  .030

INITIAL        ARO  FRACTION  .190   HCHO FRACTION  .050   ALD2 FRACTION  .000

INITIAL        NR   FRACTION  .150

NO2/NOX        .250

THERE ARE NO ALDEHYDES IN THE MECHANISM


TRANSPORTED CONCENTRATIONS

SURFACE LAYER        OZONE    .010     HYDROCARBON   .038    NOX      .000 PPM
```

```
ALOFT              OZONE    .070      HYDROCARBON   .040    NOX      .000 PPM

CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTON OF INITIAL
NON-BACKGROUND HYDROCARBON CONCENTRATION EMITTED PER HOUR)
     HOUR        1     2     3     4     5     6     7     8
     FRACTION  .170  .170  .170  .100  .020  .020  .020  .020

CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTION OF INITIAL
NON-BACKGROUND NOX CONCENTRATION EMITTED PER HOUR)
     HOUR        1     2     3     4     5     6     7     8
     FRACTION  .350  .350  .350  .190  .030  .030  .030  .070
```

```
THE FOLLOWING SIMULATIONS WERE DONE.

    HC             NOX            RATIO          O3

  .00000         .00000          .00000        .05242

  .00000         .28000          .00000        .01472

 2.00000         .28000         7.14286        .29531 NOT MAX

 2.00000         .00000          .00000        .04847

  .98209         .28000         3.50746        .07416 NOT MAX

 2.00000         .03577        55.91906        .15411 NOT MAX

 1.32266         .18517         7.14286        .25204 NOT MAX

  .66133         .09259         7.14286        .19053 NOT MAX

  .34018         .04762         7.14286        .14587 NOT MAX

  .07280         .01019         7.14286        .08800 NOT MAX

 1.79331         .28000         6.40469        .24715 NOT MAX

 1.23405         .19268         6.40469        .22353 NOT MAX

  .76652         .11968         6.40469        .19709 NOT MAX

  .38757         .06051         6.40469        .15552 NOT MAX

  .04441         .00693         6.40469        .07946 NOT MAX

 1.51773         .28000         5.42047        .18037 NOT MAX

 1.12423         .20740         5.42047        .17310 NOT MAX

  .75843         .13992         5.42047        .16909 NOT MAX

  .41532         .07662         5.42047        .15795 NOT MAX

  .03485         .00643         5.42047        .07780 NOT MAX

 1.30374         .28000         4.65620        .13291 NOT MAX

 1.04715         .22489         4.65620        .13282 NOT MAX

  .77818         .16713         4.65620        .13441 NOT MAX

  .38909         .08356         4.65620        .14591 NOT MAX

  .19455         .04178         4.65620        .12810 NOT MAX
```

```
   1.12661          .28000        4.02361          .09833 NOT MAX
   1.00531          .24985        4.02361          .10017 NOT MAX
    .50265          .12493        4.02361          .11554 NOT MAX
    .25133          .06246        4.02361          .13358 NOT MAX
    .12566          .03123        4.02361          .11569 NOT MAX
    .89566          .28000        3.19877          .06134 NOT MAX
    .44783          .14000        3.19877          .08374 NOT MAX
    .22391          .07000        3.19877          .11577 NOT MAX
    .11196          .03500        3.19877          .11544 NOT MAX
    .02417          .00756        3.19877          .08014 NOT MAX
   2.00000          .23511        8.50656          .32487 NOT MAX
   1.29516          .15225        8.50656          .25915 NOT MAX
    .64758          .07613        8.50656          .18538 NOT MAX
    .32379          .03806        8.50656          .13810 NOT MAX
    .07703          .00906        8.50656          .08569 NOT MAX
   2.00000          .19023       10.51386          .31664 NOT MAX
   1.30249          .12388       10.51386          .25081 NOT MAX
    .65124          .06194       10.51386          .17752 NOT MAX
    .32562          .03097       10.51386          .13158 NOT MAX
    .08634          .00821       10.51386          .08394 NOT MAX
   2.00000          .14534       13.76106          .29090 NOT MAX
   1.32707          .09644       13.76106          .23355 NOT MAX
    .66354          .04822       13.76106          .16599 NOT MAX
    .33177          .02411       13.76106          .12294 NOT MAX
    .10291          .00748       13.76106          .08243 NOT MAX
   2.00000          .10045       19.91038          .25119 NOT MAX
   1.37125          .06887       19.91038          .20708 NOT MAX
    .72088          .03621       19.91038          .15214 NOT MAX
    .36044          .01810       19.91038          .11309 NOT MAX
   .13666          .00686       19.91038          .08110 NOT MAX
  2.00000          .04060       49.26088          .16345 NOT MAX
  1.51839          .03082       49.26088          .14521 NOT MAX
   .95880          .01946       49.26088          .12003 NOT MAX
   .55777          .01132 [illegible].26088          .09738 NOT MAX
   .31270          .00635       49.26088          .08040 NOT MAX
   .84975          .28000        3.03481          .05527 NOT MAX
  2.00000          .00855      234.05265          .08628 NOT MAX
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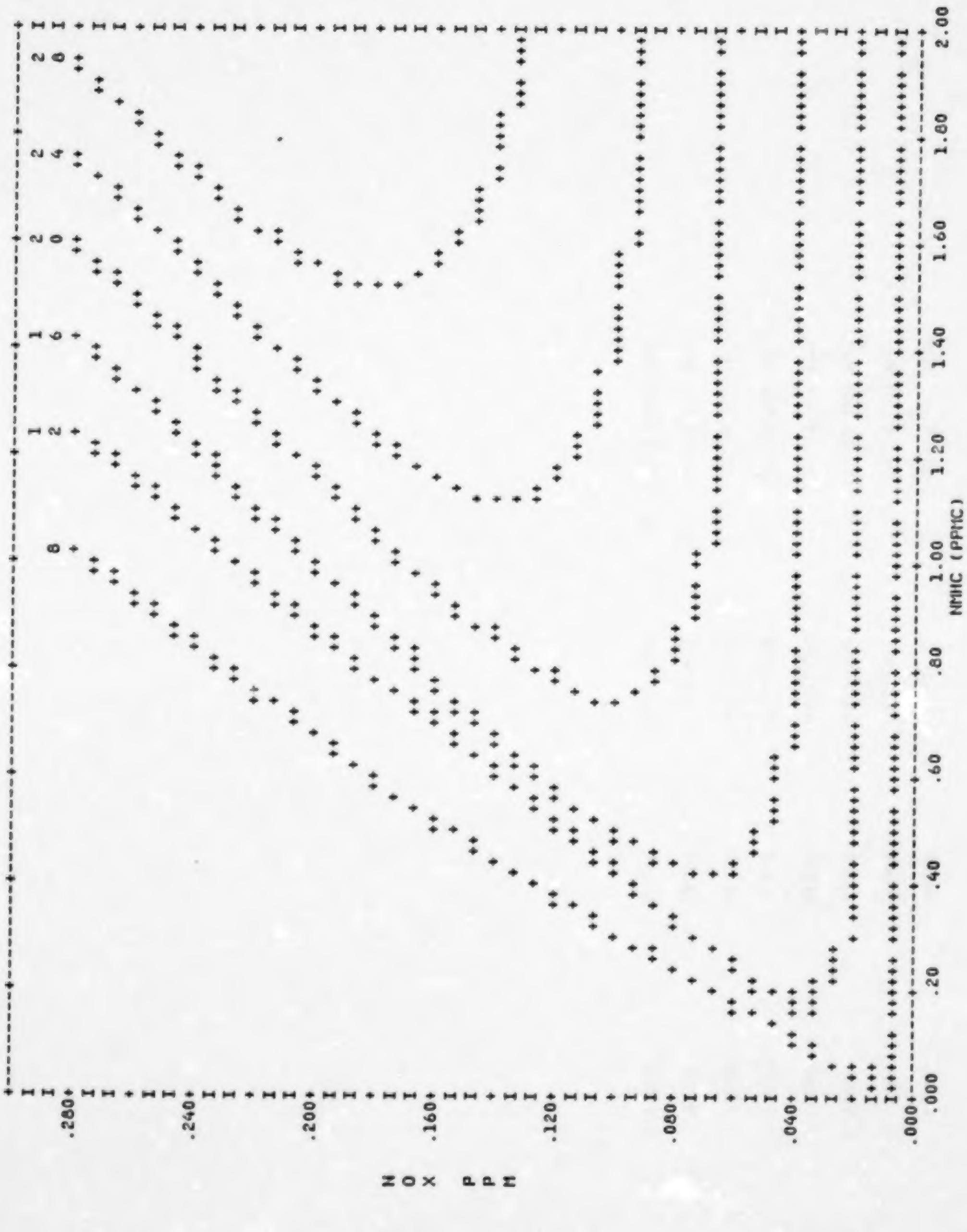
NOX PPM
.280
.240
.200
.160
.120
.080
.040
.000
NMHC (PPMC)
.000
.20
.40
.60
.80
1.00
1.20
1.40
1.60
1.80
2.00
28
24
20
16
12
8

APPENDIX G

OZIPM Output Corresponding To Inpucs Shown in Table 4-5

```
THE REACTIONS ARE

   1        NO2               =    NO     O                       1.000+00    0.000
   2        O                 =    O3                             4.400+06    0.000
   3        O3      NO        =    NO2                            2.660+01    1.450+03
   4        O3      NO2       =    NO3                            4.800-02    2.450+03
   5        O       NO2       =    NO                             1.300+04    0.000
   6        O3      OH        =    HO2                            1.000+02    1.000+03
   7        O3      HO2       =    OH                             2.400+00    1.525+03
   8        NO2     OH        =                                   1.600+04    0.000
   9        CO      OH        =    HO2                            4.400+02    0.000
  10        NO      NO        =    NO2    NO2                     1.500-04    0.000
  11        NO3     NO        =    NO2    NO2                     2.800+04    0.000
  12        NO3     NO2       =                                   2.600+01   -1.060+04
  13        HO2     NO        =    NO2    OH                      1.200+04    0.000
  14        HO2     HO2       =                                   1.500+04    0.000
  15        PAR     X         =                                   1.000+05    0.000
  16        PAR     OH        =    MEO2                           1.200+03    5.600+02
  17        OLE     O         =    MEO2   ACO3   X                2.700+03    3.250+02
  18        OLE     O         =    HCHO   PAR                     2.700+03    3.250+02
  19        OLE     OH        =    RAO2                           3.700+04   -5.400+02
  20        OLE     O3        =    HCHO   CRIG                    8.000-03    1.900+03
  21        OLE     O3        =    HCHO   MCRG   X                8.000-03    1.900+03
  22        ETH     O         =    MEO2   HO2    CO               6.000+02    8.000+02
  23        ETH     O         =    HCHO   PAR                     6.000+02    8.000+02
  24        ETH     OH        =    REO2                           1.200+04   -3.820+02
  25        ETH     O3        =    HCHO   CRIG                    2.400-03    2.560+03
  26        ACO3    NO        =    NO2    MEO2                    1.040+04    0.000
  27        RBO2    NO        =    NO2    HO2    HCHO   HCHO      1.200+04    0.000
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28    RAO2  NO     =   NO2   HO2   HCHO  HCHO   1.200+04  0.000
29    MEO2  NO     =   NO2   MEO2  HCHO  X      3.700+03  0.000
30    MEO2  NO     =   NO2   HCHO  HO2          7.400+03  0.000
31    MEO2  NO     =                            9.000+02  0.000
32    RBO2  O3     =   HCHO  HCHO  HO2          5.000+00  0.000
33    RAO2  O3     =   HCHO  HCHO  HO2          2.000+01  0.000
34    OH    HCHO   =   CRO2  X                  1.000+02  0.000
35    HCHO  OH     =   HO2   CO                 9.000+03  0.000
36    HCHO  OH     =   X     ACO3               8.200+03  0.000
37    HCHO         =   CO                       2.400-01  0.000
38    HCHO         =   QQ                       5.640-01  0.000
81    QQ           =   HO2   HO2   CO           8.667+03  0.000
82    QQ           =   MEO2  MEO2  X     XCO    1.133+03  0.000
83    XCO          =   X     CO                 1.000+04  0.000
39    ACO3  NO2    =   PAN                      7.000+03  0.000
40    PAN          =   ACO3  NO2                2.200-02  1.350+04
41    ACO3  HO2    =                            1.500+04  0.000
42    MEO2  HO2    =                            9.000+03  0.000
43    CRIG  NO     =   NO2   HCHO               1.200+04  0.000
44    CRIG  NO2    =   NO3   HCHO               8.000+03  0.000
45    CRIG  HCHO   =                            2.000+03  0.000
46    MCRG  NO     =   NO2   HCHO  PAR          1.200+04  0.000
47    MCRG  NO2    =   NO3   HCHO  PAR          8.000+03  0.000
48    MCRG  HCHO   =                            2.000+03  0.000
49    CRIG         =   CO                       6.700+02  0.000
50    CRIG         =                            2.400+02  0.000
51    CRIG         =   HO2   HO2   CO           9.000+01  0.000
52    MCRG         =                            1.500+02  0.000
53    MCRG         =   MEO2  OH    CO           3.400+02  0.000
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54    MCRG          =   MEO2   HO2                     4.250+02   0.000
55    MCRG          =   HCHO   HO2    HO2     CO       8.500+01   0.000
56    ARO     OH    =   RARO                           6.000+03   6.000+02
57    ARO     OH    =   HO2    OPEN                    1.450+04   4.000+02
58    RARO    NO    =   NO2    PHEN   HO2              4.000+03   0.000
59    OPEN    NO    =   NO2    ALD2   X       APRC     6.000+03   0.000
60    APRC          =   ALD2   HCHO   CO      X        1.000+04   0.000
61    APRC          =   HCHO   HCHO   CO      CO       1.000+04   0.000
62    PHEN    NO3   =   PHO    HNO3                    5.000+03   0.000
63    PHO     NO2   =                                  4.000+03   0.000
64    PHO     HO2   =   PHEN                           5.000+04   0.000
65    OPEN    O3    =   ALD2   X      APRC             4.000+01   0.000
66    OH      PHEN  =   HO2    APRC   PAR     HCHO     3.000+04   0.000
67    ALD2          =   HO2    ACO3   CO               2.000-02   0.000
68    PHEN    OH    =   PHO                            1.000+04   0.000
69    CRO2    NO    =   NO2    HCHO   ACO3    X        1.200+04   0.000
70    ALD2    OH    =   ACO3   CO                      2.500+04   0.000
71    HONO          =   OH     NO                      3.100+00   0.000
72    OH      NO    =   HONO                           9.770+03   0.000
73    O3            =   O1D                            5.400-01   0.000
74    O1D           =   O                              4.440+10   0.000
75    O1D           =   OH     OH                      6.800+09   0.000
90    OH            =   HO2                            8.800+01   0.000
91    OH            =   MEO2                           2.800+01   0.000
92    NR            =   NR                             1.000+00   0.000
99    O3            =   O                              1.000+00   0.000
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PHOTOLYTIC RATE CONSTANTS CALCULATED FOR

        CITY NAME

LATITUDE      39.900

LONGITUDE      75.100

TIME ZONE     5.0

DATE          6      24    1980

TIME          800    TO    1800      LOCAL DAYLIGHT TIME


DILUTION DETERMINED FROM THE FOLLOWING

INVERSION HEIGHTS      INITIAL   250.     FINAL      1235.

TIMING                 START     800.     STOP       1617.


MIXING HEIGHTS (AT THE BEGINNING OF EACH HOUR)

TIME        800     900    1000    1100    1200    1300    1400    1500    1600    1700

HEIGHT    250.0   411.5   614.3   804.4   945.1  1044.5  1117.5  1174.3  1222.1  1235.0


INITIAL          PAR  FRACTION  .580   ETH  FRACTION  .040   OLE  FRACTION  .030

INITIAL          ARO  FRACTION  .190   HCHO FRACTION  .050   ALD2 FRACTION  .000

INITIAL          NR   FRACTION  .150

NO2/NOX       .250

THERE ARE NO ALDEHYDES IN THE MECHANISM


TRANSPORTED CONCENTRATIONS

SURFACE LAYER         OZONE    .010      HYDROCARBON   .038    NOX       .000 PPM
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ALOFT              OZONE    .060     HYDROCARBON   .024    NOX      .000 PPM

CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTON OF INITIAL
NON-BACKGROUND HYDROCAPBON CONCENTRATION EMITTED PER HOUR)
    HOUR        1     2     3     4     5     6     7     8
    FRACTION  .170  .170  .170  .100  .020  .020  .020  .020

CONTINUOUS EMISSIONS (EXPRESSED AS THE FRACTION OF INITIAL
NON-BACKGROUND NOX CONCENTRATION EMITTED PER HOUR)
    HOUR        1     2     3     4     5     6     7     8
    FRACTION  .350  .350  .350  .190  .030  .030  .030  .070
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THE FOLLOWING SIMULATIONS WERE DONE.

   HC              NOX             RATIO           O3

  .00000          .00000           .00000         .04539
  .00000          .28000           .00000         .01235
 2.00000          .28000          7.14286         .28355 NOT MAX
 2.00000          .00000           .00000         .04185
 1.00000          .28000          3.57143         .06664 NOT MAX
 2.00000          .04419         45.25853         .16663 NOT MAX
 1.35425          .18960          7.14286         .24271 NOT MAX
  .67713          .09480          7.14286         .18331 NOT MAX
  .37169          .05204          7.14286         .14301 NOT MAX
  .07044          .00986          7.14286         .08059 NOT MAX
 1.80791          .28000          6.45682         .23737 NOT MAX
 1.27575          .19758          6.45682         .21298 NOT MAX
  .82427          .12766          6.45682         .18879 NOT MAX
  .44550          .06900          6.45682         .15389 NOT MAX
  .06409          .00993          6.45682         .08031 NOT MAX
 1.55179          .28000          5.54209         .17523 NOT MAX
 1.17901          .21274          5.54209         .16574 NOT MAX
  .82899          .14958          5.54209         .15766 NOT MAX
  .49410          .08915          5.54209         .15070 NOT MAX
  .06131          .01106          5.54209         .08216 NOT MAX
 1.35173          .28000          4.82760         .13096 NOT MAX
 1.11191          .23032          4.82760         .12761 NOT MAX
  .86316          .17880          4.82760         .12606 NOT MAX
  .58884          .12197          4.82760         .12745 NOT MAX
  .29442          .06099          4.82760         .12969 NOT MAX
  1.18467          .28000        4.23096          .09793 NOT MAX
  1.07582          .25427        4.23096          .09787 NOT MAX
   .94544          .22346        4.23096          .09828 NOT MAX
   .47272          .11173        4.23096          .10707 NOT MAX
   .26525          .06269        4.23096          .12031 NOT MAX
  1.08201          .28000        3.86431          .07999 NOT MAX
   .54100          .14000        3.86431          .08967 NOT MAX
   .27050          .07000        3.86431          .10990 NOT MAX
   .13525          .03500        3.86431          .10832 NOT MAX
   .04485          .01161        3.86431          .08173 NOT MAX
  2.00000          .23559        8.48950          .31765 NOT MAX
  1.31960          .15544        8.48950          .25434 NOT MAX
   .65980          .07772        8.48950          .18006 NOT MAX
   .32990          .03886        8.48950          .13231 NOT MAX
   .10162          .01197        8.48950          .08520 NOT MAX
  2.00000          .19117       10.46189          .31208 NOT MAX
  1.32491          .12664       10.46189          .24788 NOT MAX
   .66246          .06332       10.46189          .17315 NOT MAX
   .33123          .03166       10.46189          .12632 NOT MAX
   .11262          .01076       10.46189          .08449 NOT MAX
  2.00000          .14676       13.62815          .28763 NOT MAX
  1.34983          .09905       13.62815          .23209 NOT MAX
   .69305          .05085       13.62815          .16472 NOT MAX
   .34653          .02543       13.62815          .11982 NOT MAX
   .13245          .00972       13.62815          .08310 NOT MAX
  2.00000          .10234       19.54268          .24927 NOT MAX
  1.39522          .07139       19.54268          .20661 NOT MAX
   .75571          .03867       19.54268          .15209 NOT MAX
   .37785          .01933       19.54268          .11090 NOT MAX
  .17127        .00876     19.54268      .08174 NOT MAX
 1.53933        .03401     45.25853      .14806 NOT MAX
  .99261        .02193     45.25853      .12189 NOT MAX
  .60068        .01327     45.25853      .09862 NOT MAX
  .35861        .00792     45.25853      .08104 NOT MAX
  .90860        .28000      3.24501      .05401 NOT MAX
 2.00000        .01351    148.03663      .09809 NOT MAX
```

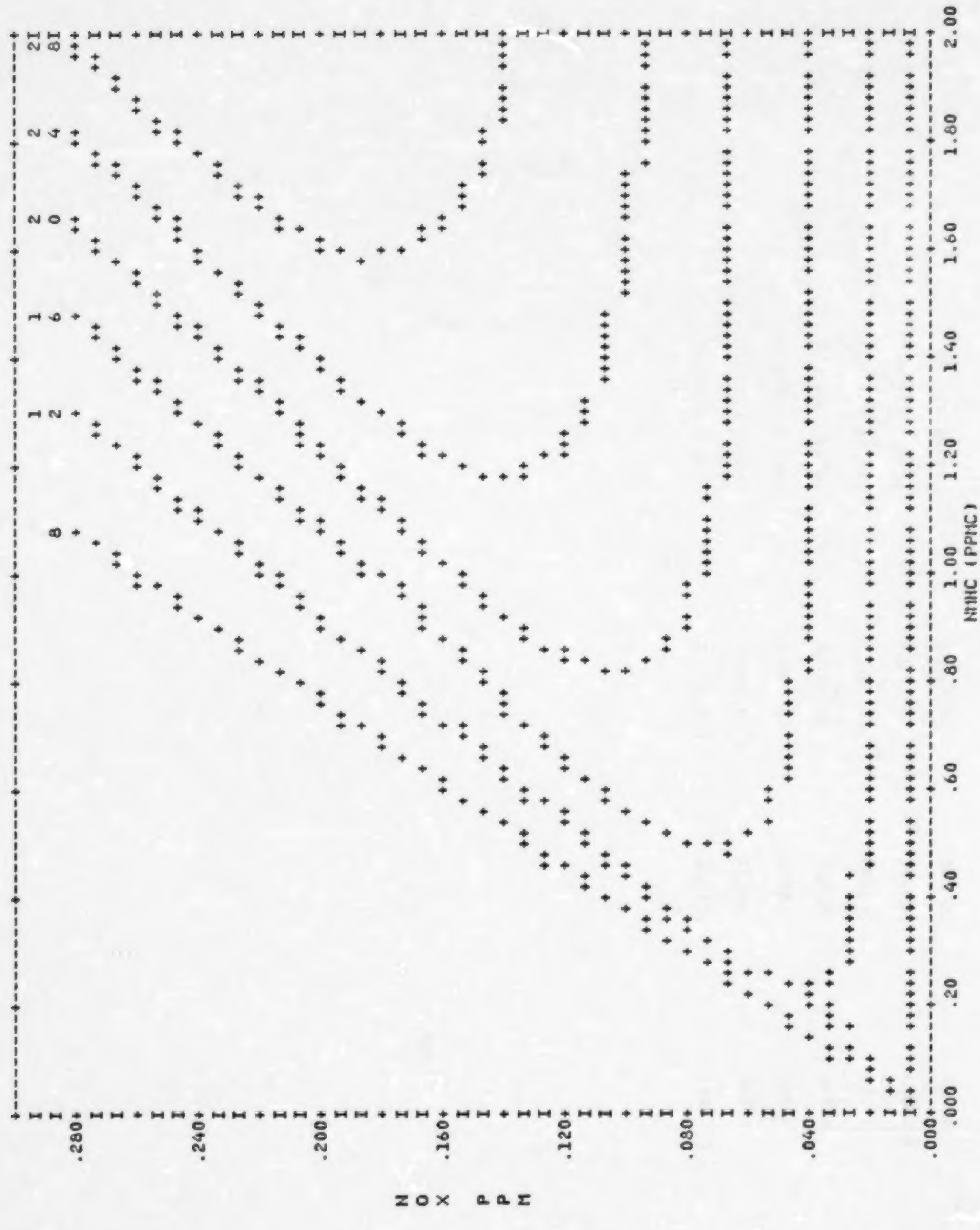
NOX PPM
.000
.040
.080
.120
.160
.200
.240
.280
NMHC (PPMC)
.000
.20
.40
.60
.80
1.00
1.20
1.40
1.60
1.80
2.00
8
12
16
20
24
28

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THE O3   LINES ARE    .08000  .12000  .16000  .20000  .24000  .28000
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